

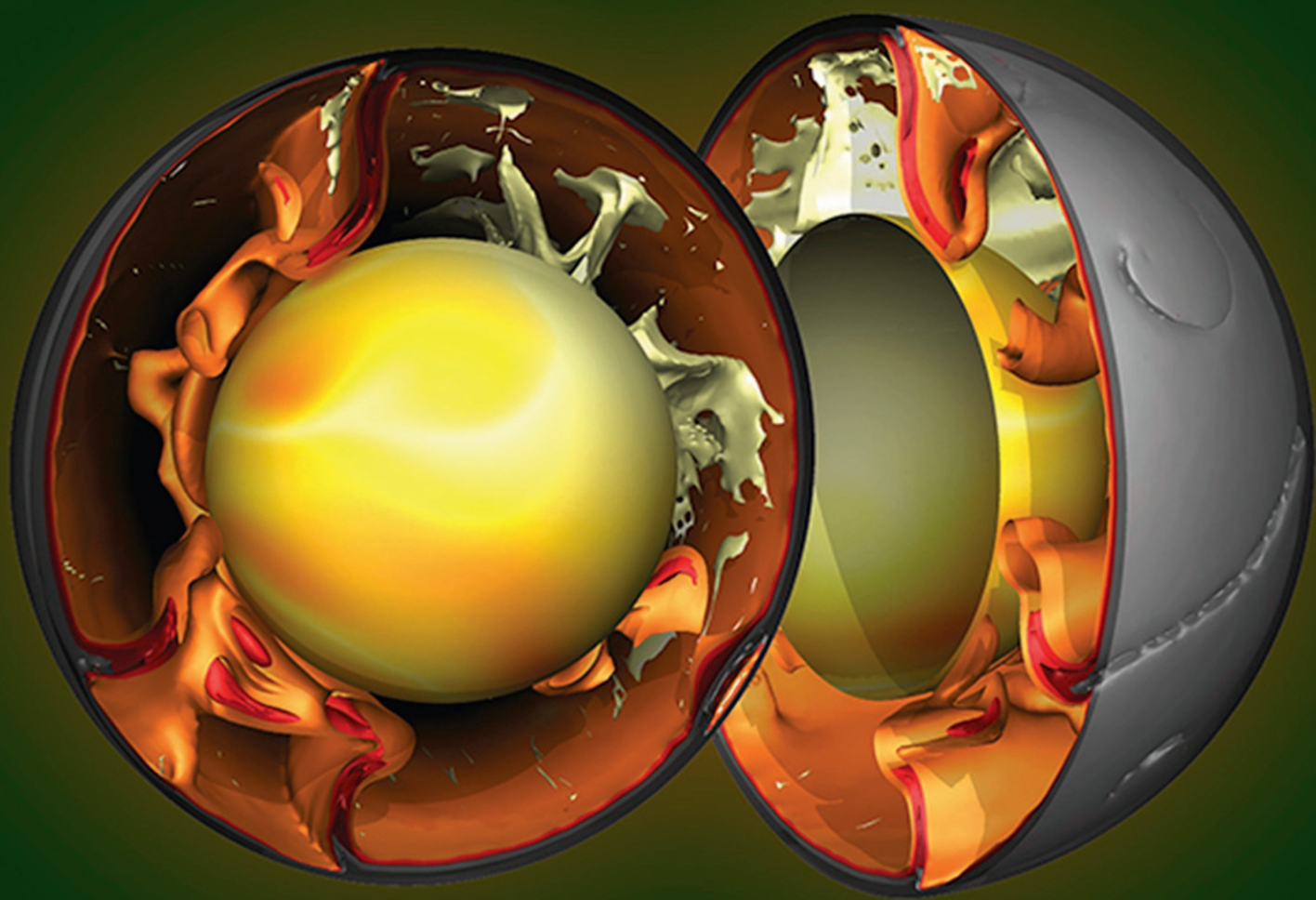


SECOND EDITION

TREATISE ON GEOPHYSICS

Volume 2

MINERAL PHYSICS



VOLUME EDITORS: DAVID PRICE AND LARS STIXRUDE
EDITOR-IN-CHIEF: GERALD SCHUBERT

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VOLUME 2

MINERAL PHYSICS

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PREFACE

The *Treatise on Geophysics* is a comprehensive and in-depth study of the physics of the Earth and of terrestrial-like planets residing both within and outside our solar system. Its breadth and detail of coverage are beyond what any single geophysics text can provide. The first edition of the *Treatise on Geophysics* was published in 2007, nearly a decade ago. Of course, there is much progress in science in that length of time and the field of geophysics has grown rapidly and developed new lines of inquiry. Accordingly, we have brought the *Treatise on Geophysics* up-to-date with this second edition. The new edition will continue to provide students and professionals with fundamental and state-of-the-art discussion of all aspects of geophysics. In this new edition, the reader will find updates to all the chapters contained in the first edition and new chapters that discuss topics missing from the first edition. In a few instances, chapters from the first edition have simply been reprinted in order to avoid gaps in coverage. Chapters that emphasized fundamental physics often required little updating.

A highlight of the second edition is a new volume on Resources in the Near-Surface Earth. The new volume discusses the role of geophysics in the exploitation and conservation of natural resources and the assessment of degradation of natural systems by pollution. The near surface is a zone where humans and natural systems interact. Understanding the effects of human impacts is a challenge particularly for the long term.

There are four new chapters in the volume on Deep Earth Seismology. One of them describes progress in seismic instrumentation in the last 30 years in the era of broadband digital sensor and recording systems. Another one addresses a new approach for the determination of crust and uppermost mantle structure, based on ambient noise cross-correlations. This has revolutionized the field, since it allows the study of regional structure at high resolution in areas where there are no earthquakes. The third new chapter is devoted to recent advances in characterizing the lithosphere–asthenosphere boundary under both oceans and continents. Finally, the last new chapter discusses the morphology of subducted slabs in the Earth’s transition zone.

The Mineral Physics volume has new chapters on dynamic (shock-wave) compression methods, and on the mineralogy of the upper mantle and the D'' layer focusing on post-perovskite, and extrasolar super-Earths.

New material in the Geodesy volume expands the temporal resolution and latency of geodetic measurements to high-rate, real-time measurements and increases the spatial resolution to meter size pixels with optical and radar imaging systems. Application areas are extended with new material on the uses of Earth gravity measurements.

The Earthquake Seismology volume has a new chapter on rock mechanics that is a comprehensive account of modern rock mechanics with emphasis on the variation of frictional properties of rocks during an earthquake cycle. Many chapters have considerable updates reflecting the lessons from significant recent earthquakes (e.g., the 2011 Tohoku-Oki earthquake and the 2013 Okhotsk deep earthquake), new observations on slow slips and triggered earthquakes, and developments of new methods (e.g., back projection method). Some chapters are updated (e.g., paleoseismology and strong ground motion) with substantial new material.

Chapters in the Geomagnetism volume have been updated to include recent advances in the acquisition of larger data sets and higher quality data and in the construction of more reliable and sophisticated models. Improvements in data have occurred in areas such as magnetic anomalies, paleointensities, and planetary magnetism. Improvements in models of the present day field include so-called comprehensive models and models that incorporate data assimilation.

The Crustal and Lithosphere Dynamics volume has new contributions on mountain building and landscape evolution.

The Mantle Dynamics volume contains new chapters on the generation of plate tectonics from mantle convection and the core–mantle boundary region.

The Core Dynamics volume features a comprehensive update of this rapidly changing subject, including new chapters on turbulence and waves in the fluid outer core.

The volume on the Evolution of the Earth presents a new assessment on the role of volatiles in Earth evolution.

There are new chapters in the Physics of Terrestrial Planets and Moons volume on planetary atmospheres, planetary tectonics, extrasolar planets and asteroids and comets. The study of extrasolar planets has had explosive growth in the last decade and new spacecraft missions have significantly enhanced our knowledge of solar system planets and moons.

Finally, this is an opportunity for me to thank and acknowledge the editors of the individual volumes for their hard work, patience, dedication, and commitment in bringing this new edition of the Treatise to fruition. I am also indebted to Gemma Tomalin of Elsevier for her care and attention to the organization and production of the Treatise and to Deepa Arumugam for her careful coordination of the proofs from the copyeditor and typesetter. Of course, the authors of the individual chapters are the ones who are responsible for the excellence of the Treatise. We have all had some ups and downs in the process of producing the second edition of the Treatise but the final product is one that we can all view with pride.

Gerald Schubert
Editor-in-Chief

EDITOR-IN-CHIEF



Gerald Schubert is Distinguished Professor Emeritus in the Department of Earth, Planetary and Space Sciences at the University of California, Los Angeles. His research interests encompass the physics of the interiors and atmospheres of the Earth, the Moon, and the other moons and planets of the solar system. He is co-author with Donald Turcotte of *Geodynamics* (ed. 3, Cambridge University Press, 2014) and with Turcotte and Peter Olson of *Mantle Convection in the Earth and Planets* (Cambridge University Press, 2001). He is the author of over 540 research papers. He has participated in a number of NASA's planetary missions, including Apollo, Pioneer Venus, Magellan, and Galileo, and has been editor and editorial board member of many journals, including *Icarus*, *Journal of Geophysical Research*, *Geophysical Research Letters*, and *Annual Reviews of Earth and Planetary Sciences*. Professor Schubert is a Fellow of the American Geophysical Union and a recipient of the Union's James B. MacElwane medal and the Harry H. Hess medal. He is a member of the National Academy of Sciences and the American Academy of Arts and Sciences.

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2.01 Mineral Physics: An Introduction and Overview

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Mineral physics involves the application of physics and chemistry techniques in order to understand and predict the fundamental behavior of Earth materials (e.g., Kieffer and Navrotsky, 1985) and hence provide solutions to large-scale problems in Earth and planetary sciences. Mineral physics, therefore, is relevant to all aspects of solid Earth sciences, from surface processes and environmental geochemistry to the deep Earth and the nature of the core. In this volume, however, we focus only on the geophysical applications of mineral physics (see also Ahrens, 1995; Hemley, 1998; Poirier, 2000). These applications, however, not only are constrained to understanding the structure of the Earth (see Volume 1) and its evolution (see Volume 9) but also will play a vital role in our understanding of the dynamics and evolution of other planets in our solar system (see Volume 10 and Oganov et al., 2005).

As a discipline, mineral physics as such has only been recognized for some 30 years or so, but in fact, it can trace its origins back to the very foundations of solid Earth geophysics itself. Thus, for example, the work of Oldham (1906) and Gutenberg (1913), which defined the seismological characteristics of the core, led to the inference on the basis of materials physics that the outer core is liquid because of its inability to support the promulgation of shear waves.

A landmark paper in the history of the application of mineral physics to the understanding of the solid Earth is the *Density of the Earth* by Williamson and Adams (1923). Here, the elastic constants of various rock types were used to interpret the density profile as a function of depth within the Earth that had been inferred from seismic and gravitational data. Their work was marked by taking into account the gravitationally induced compression of material at depth within the Earth, which is described by the Williamson–Adams relation that explicitly links geophysical observables ($g(r)$, the acceleration due to gravity as a function of radius, r , and the longitudinal and shear seismic wave velocities, V_p and V_s) with mineral properties (K_s , the adiabatic bulk modulus, and density, ρ), via

$$\frac{d\rho(r)}{\rho(r)} = -\frac{g(r)dr}{\varphi(r)}$$

where $\phi(r)$ is the seismic parameter as a function of radius, given by

$$\varphi(r) = V_p^2(r) - \frac{4}{3}V_s^2(r) = \frac{K_s(r)}{\rho(r)}$$

Further progress in inferring the nature of the Earth's deep interior rested upon experimental determination of the elastic properties of rocks and minerals as a function of pressure and temperature. Notably, this work was pioneered over several decades by Bridgman (1931). In parallel with experimental studies, however, a greater understanding of the theory behind the effect of pressure on compressibility was made by Murnaghan (1937) and Birch (1938). These insights into

the equations of state of materials enabled Birch (1952) (see Figure 1) to write his classic paper entitled *Elasticity and the Constitution of the Earth's Interior*, which laid the foundations of our current understanding of the composition and structure of our planet.

One notable outcome from the investigation of the effect of pressure and temperature on material properties was the discovery of new high-density polymorphs of crustal minerals. Thus, Coes (1953) synthesized a new high-density polymorph of SiO_2 (subsequently named coesite), and Ringwood (1959) reported the synthesis of the spinel-structured Fe_2SiO_4 (which had previously been predicted by Bernal, 1936). Ringwood and colleagues went on to make a variety of other high-density silicate polymorphs, including the phases that are now thought to make up the transition zone of the mantle, namely, the spinelloids wadsleyite ($\beta\text{-Mg}_2\text{SiO}_4$) and ringwoodite ($\gamma\text{-Mg}_2\text{SiO}_4$), and the garnet-structured polymorph of MgSiO_3 majorite. Further insights into the probable nature of deep Earth minerals came from Stishov and Popova (1961), who synthesized the rutile-structured polymorph of SiO_2 (stishovite) that is characterized by having Si in octahedral coordination, and from Takahashi and Bassett (1964), who first made the hexagonal close-packed polymorph of Fe, which is today thought to be the form of Fe to be found in the Earth's core (but see Chapter 2.06). As high-pressure and high-temperature experimental techniques evolved, still further phases were discovered, the most important of which was the perovskite-structured polymorph of MgSiO_3 (Liu, 1975). It was thought for some time that this discovery and the subsequent work on the details of the high-pressure phase diagrams of silicate minerals had enabled a robust mineralogical model for the mantle to be established. More recently, this view, however, has had to be revised, after the discovery of a 'post-perovskite' phase (Murakami et al., 2004; Oganov and Ono, 2004; Tsuchiya et al., 2004), which may be stable in the deepest part of the lower mantle (Chapter 2.05).

Notwithstanding, however, the possibility of further new discoveries, the mineralogy, and composition of the mantle and the core are now relatively well defined. The current view of the mineralogy of the mantle is summarized in Figure 2, while as suggested by Birch (1952), the core is considered to be composed of iron (with minor amounts of nickel) alloyed with light elements (probably O, S, and/or Si). The solid inner core is crystallizing from the outer core and so contains less light elements. The current status of our understanding of the nature of the deep Earth is reviewed in detail in Chapters 2.03–2.05. Chapter 2.02 provides a general overview of the structure of the mantle. The nature of the lower mantle is still relatively controversial, since generating lower mantle pressures (~ 25 – 130 GPa) and temperatures (~ 2000 – 3000 K) is still experimentally challenging, and mineral physics data and phase relations for the minerals thought to be found here are less robust. Furthermore, the discovery of the postperovskite phase



Figure 1 Francis Birch (1903–92), Royal Astronomical Society medalist 1960; Bowie medalist 1960. Courtesy AIP Emilio Segrè Visual Archives.

has added even greater uncertainty to the nature of the D'' zone and the core–mantle boundary. The problems of the lower mantle and the core–mantle boundary are therefore reviewed in [Chapter 2.03](#). Although the major element chemistry of the mantle is quite well studied, it is probably fair to say that the understanding of the trace element chemistry and the role of volatiles in the deep mantle is still in its infancy. This aspect of mantle chemistry, however, is vital if we are fully to understand the processes involved in planetary formation, core segregation, and subsequent evolution of the Earth (see Volumes 9 and 10). [Chapter 2.04](#) provides a review of our understanding of this aspect of the mantle, while the considerable progress in our understanding of the nature and evolution of the core is provided in [Chapter 2.05](#).

As indicated earlier, our understanding of the lower mantle and core is limited to some extent by our inability to easily reproduce the high-pressure and high-temperature conditions in planetary interiors. To obtain greater insight, theory and experiment must be used together, and [Chapters 2.08](#) and [2.15](#) present reviews of the theory underlying high-pressure, high-temperature physics, and the major experimental methods that are being developed to probe this parameter space. [Chapter 2.08](#) outlines the thermodynamic basis behind high-pressure and high-temperature behavior and expands in greater detail on equations of state and the way in which the density and elastic properties of materials respond to changes in pressure and temperature. The macroscopic behavior of minerals depends upon the microscopic or atomistic interactions within the mineral structure. Thus, for example, free energy (and eventually phase stability) depends in part upon entropy, which in turn is dominated (for silicates at least) by lattice vibrations. Hence, in [Chapter 2.09](#), a detailed analysis of lattice vibrations and spectroscopy of mantle minerals is

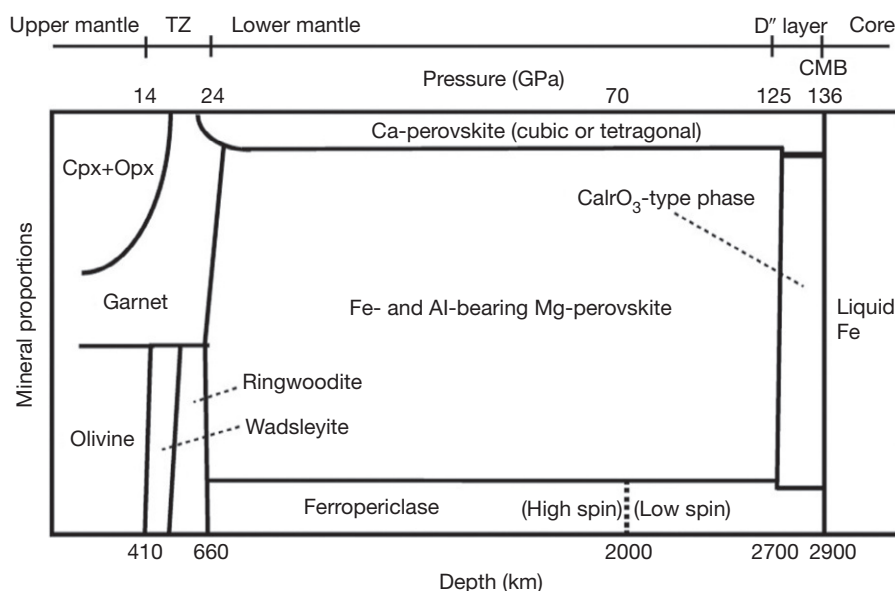


Figure 2 Phase relations of pyrolitic mantle composition as a function of depth. Reproduced from Ono S and Oganov AR (2005) In situ observations of phase transition between perovskite and CaIrO_3 -type phase in MgSiO_3 and pyrolitic mantle composition. *Earth and Planetary Science Letters* 236, 914–932. Courtesy AIP Emilio Segrè Visual Archives.

presented. For the past 20 years, advances in computing power have enabled computational mineral physics to make a contribution to our understanding of the thermodynamic, thermoelastic, and dynamical properties of high-pressure minerals. Initially, the results of simulations based on interatomic potentials provided semiquantitative insights into, for example, the lattice vibrations and the thermodynamics of mantle phases (e.g., Price et al., 1987; Wall and Price, 1988). But more recently, quantum mechanical simulations of mantle and core phases have been able to achieve a precision and accuracy comparable with that achievable experimentally, and as such, *ab initio* modeling must now be seen as a legitimate complement to experimental study. Therefore, in this volume, the theory and results from *ab initio* studies of some deep Earth phases are reviewed in Chapter 2.15.

Despite the power and insight provided by theory, mineral physics is dependent upon quantitative high-pressure and high-temperature experimental results. Such work was pioneered by Williamson, Adams (Figure 3), and Bridgman and then was taken up by others such as Ringwood, Bassett, Liu, and many groups in Japan (see, e.g., Akimoto, 1987 and Figure 4), but in the past 30 years, huge advances have been made and today, for

example, laser-heated diamond anvil cells can be used to access temperatures and pressures up to ~ 6000 K and 250 GPa. Such experiments, however, can only be carried out on very small sample volumes and for very short periods of time. Multianvil experiments can be used to study much larger volumes of material and are stable over a longer time interval. These techniques are, therefore, complementary and are both developing rapidly. Chapter 2.10 provides a review of multianvil cell methods, while Chapter 2.11 gives an analysis of diamond anvil cell techniques. A third technique for producing high pressures and temperatures is via shock compression, reviewed in Chapter 2.16. In this approach, a high-velocity impact is produced by firing a projectile at a mineral target. Very high-pressure and shock-produced heating can be obtained, but only for a few 100 ns; however, this is sufficient in many applications to enable the measurement of the pressure, density, and energy of the shocked state and in certain cases to interrogate the atomic structure and bonding of the material.

Achieving the high pressures and temperatures that occur in the deep Earth is, however, just the beginning of the challenge that faces experimental mineral physicists, since it is also necessary to measure a variety of physical properties under these conditions. Therefore, in Chapters 2.12–2.14, the specific techniques for measuring elastic and acoustic properties, electronic and magnetic properties, and rheological properties are described in greater detail.



Figure 3 Leason Heberling Adams (1887–1969), American Geophysical Union (AGU) president 1944–47, Bowie medalist 1950. Courtesy AIP Emilio Segrè Visual Archives.

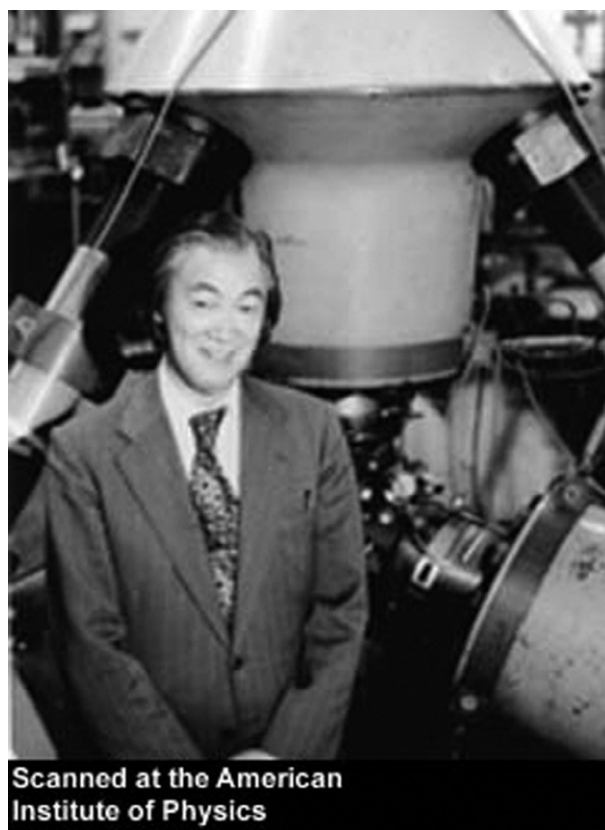


Figure 4 Syun-iti Akimoto (1925–2004), Royal Astronomical Society medalist 1983, Bowie medalist 1983. Courtesy AIP Emilio Segrè Visual Archives.

One of the long-term goals of mineral physics research is to enable a full interpretation of seismic tomographic data (see Volume 1) and to provide a three-dimensional description of the mineralogy, composition, and thermal structure of the Earth's deep interior (Stixrude and Lithgow-Bertelloni, 2012). To this end, we need not only full descriptions of the seismic properties of rocks and minerals, as a function of composition, pressure, and temperature (see Chapter 2.02), but also an understanding of the nature and origin of anisotropy in the Earth (see Chapter 2.20) and the significance and reasons for seismic wave attenuation (see Chapter 2.17).

In addition to being able to invert seismic data to provide an instantaneous picture of the Earth's interior, we desire to be able to describe the dynamic evolution of our planet (see Volumes 7 and 8). As such, we need to be able to constrain, for example, geodynamical models of mantle convection, with the appropriate rheological descriptions of mantle phases (see Chapter 2.14), and self-consistent descriptions of heat flux and planetary thermal structure. Key to the latter is our understanding of thermal conductivity at high pressures and temperatures, which is an area where theory and experiment are still evolving and much progress is still required (see Chapter 2.22). Similarly, our ability to describe the dynamics of core convection, and hence the geodynamo, is critically dependent on our understanding of the physical properties of liquid and solid iron under core conditions (see Chapters 2.06, 2.13, and 2.19).

One particular problem in our understanding of the Earth is the nature of the core–mantle boundary (Lay et al., 2008). It has been variously suggested, for example, that it is a 'grave yard' for subducted slabs, is a reaction zone with the core, is associated with a postperovskite phase change, is the location of pods of partially molten material, is enriched in iron, and is the source of deep mantle plumes (see Volume 7). To establish the importance of some of these hypotheses requires not only high-quality seismic data but also tight constraints on the thermal structure of the core and the high-pressure melting behavior of mantle and core material (see Chapter 2.22). The melting of mantle material also obviously plays a vital role in volcanism and planetary evolution (Stixrude et al., 2009). The migration of melts and their eruption or injection into the crust is central to our understanding of the dynamics of the upper mantle. The properties of melts are discussed in Chapter 2.19.

Another long-standing problem in geophysics is the energetics of the core and the driving force behind the geodynamo (see Volume 8). To be able to model this process, accurate descriptions of the melting of iron and the chemical compositions of the inner and outer core are essential (e.g., Nimmo et al., 2004). The possible presence of radioactive elements in the core (such as ^{40}K) would be highly significant as such internal sources of heat would greatly influence the cooling rate of the core and hence the age and rate of growth of the inner core; but it is still an open question. The stability of the geodynamo may also be affected by thermal and electrical coupling with the mantle; hence, we need to fully understand the electrical properties of mantle phases (see Chapter 2.25). Finally, for example, insights into the past nature of the geodynamo, as its paleointensity, can only be obtained from paleomagnetic data (see Volume 5), which requires a detailed understanding of rock minerals and magnetism (see Chapter 2.24).

In the following chapters in this volume, the great progress that has been made in our understanding of the physics and chemistry of minerals is clearly laid out. However, each author also highlights a number of issues that are still outstanding or that need further work to resolve current contradictions. The resolution of some of the problems outlined earlier and in the subsequent chapters will depend on more precise or higher-resolution geophysical measurements (e.g., the exact density contrast between the inner and outer core), while others will be solved as a result of new experimental or computational techniques. The combination, for example, of intense synchrotron radiation and neutron sources with both diamond anvil and multianvil cell devices promises to yield much more information on high-pressure seismic (or equivalently elastic) properties of deep Earth phases. In the foreseeable future, developments in anvil design will see large-volume devices that can be used to determine phase equilibria to 100 GPa or to study high-pressure rheology to 30 GPa and beyond. But more predictably, the continued development of increasingly powerful computers will see the role of computational mineral physics grow still further, as the study of more complex problems (like rheology and thermal transport) becomes routine. In addition, the use of more sophisticated *ab initio* methods (like quantum Monte Carlo techniques) will become possible, and accurate studies of the band structure and electrical properties of iron bearing silicates will be performed. Finally, the pressures of the Earth's interior (up to 360 GPa) do not represent the limit of interest for mineral physicists. Already extrasolar system, giant, Earth-like planets are being considered, and understanding their internal structure will open up even greater challenges as discussed in Chapter 2.07.

In conclusion, therefore, this volume contains a comprehensive review of our current state of understanding of mineral physics, but without doubt, there is still much that is unknown, but the prospect for further progress is excellent, and it is certain that in the next decades, many issues, which are still controversial today, will have been resolved.

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2.02 Mineralogy of the Earth: Phase Transitions and Mineralogy of the Upper Mantle

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2.02.1 Introduction

The Earth's upper mantle extends from the base of the crust down to about 410 km where a discontinuity marks the boundary to the transition zone. Knowledge of the mineralogical composition of the upper mantle is essential to derive the density structure of the upper mantle for the interpretation of geophysical data. The knowledge of the composition and the mineralogy of the upper mantle, and therefore its physical and chemical properties, stem from both indirect investigations (e.g., experiments at P and T conditions relevant to the upper mantle and theoretical calculations) and direct petrologic and geochemical investigations of tectonically exposed mantle rocks, abyssal peridotites, and mantle xenoliths. Compared to the Earth's crust, which consists of hundreds of different minerals and quite a few different rock types (Rudnick and Gao, 2003), the chemical and mineralogical composition of the Earth's mantle is rather straightforward. We know that most of the upper mantle consists of peridotite, a rock type that is composed of four main minerals only (Figure 1): olivine $(\text{Mg,Fe})_2\text{SiO}_4$, orthopyroxene $(\text{Mg,Fe})_2\text{Si}_2\text{O}_6$, clinopyroxene $\text{Ca}(\text{Mg,Fe})\text{Si}_2\text{O}_6$, and mostly an aluminous phase (either plagioclase, spinel, or garnet as a function of pressure).

In this chapter, we focus on the chemical and mineralogical composition of the upper mantle, with particular emphasis on the effect of variable bulk compositions on subsolidus phase

relations. We will first briefly discuss the *chemical composition* of the mantle, taking into account information mainly from natural mantle rocks (i.e., xenoliths, ophiolites, orogenic peridotites, and abyssal peridotites) and experimental simulations. We will then discuss the *mineralogical composition* of the upper mantle in the context of its chemical composition, with a special focus on subsolidus phase relations and phase transformations. Here, most of the data originate from high-pressure high-temperature experiments, with some additional information from natural mantle rocks and thermodynamic modeling.

The concluding sections deal with the mineralogical composition of the upper mantle in subduction zones, with particular emphasis on the role of hydrous phases in the sub-subduction zone mantle as they control the transport and release of water at depth. Phase relations in metasomatized lherzolite will also be addressed, focusing on the role of potassic phases stable at mantle pressures and temperatures.

2.02.2 Chemical and Mineralogical Composition of the Upper Mantle

The *chemical* and *mineralogical* composition of the upper mantle may directly be studied using petrologic and field-based observations on naturally occurring mantle rocks, such as

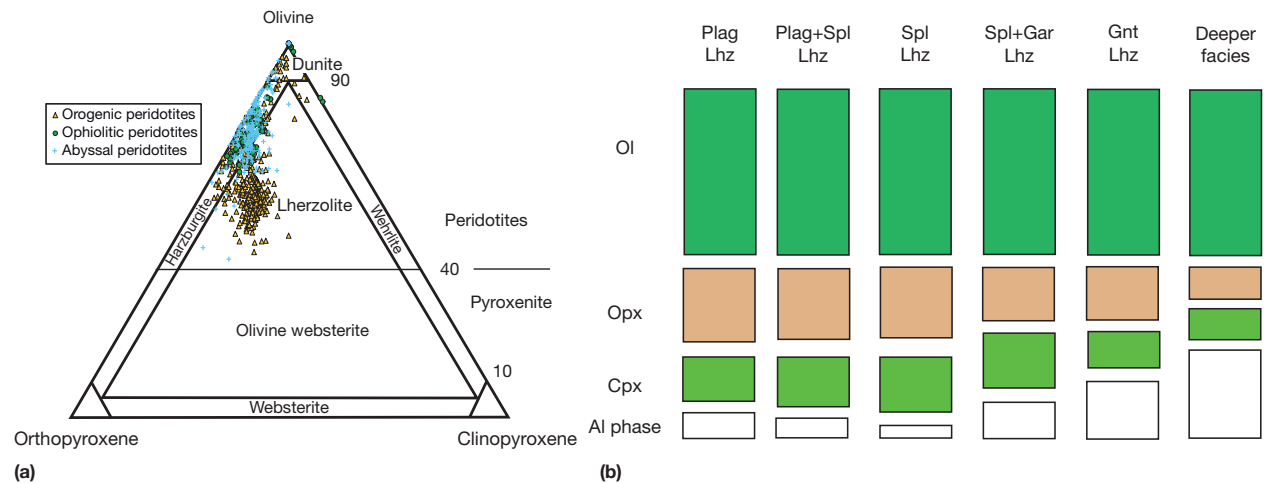


Figure 1 (a) Nomenclature of ultramafic rocks as a function of modal abundances of olivine, orthopyroxene, and clinopyroxene. Modal compositions of orogenic, ophiolitic, and abyssal mantle peridotites are from review data in Bodinier and Godard (2003) (Left modified from Bodinier J-L and Godard M (2003) Orogenic, Ophiolitic, and Abyssal Peridotites. In Carlson RW (ed.) *Treatise on Geochemistry, The Mantle and the Core*, pp. 103–170. Amsterdam: Elsevier.); (b) schematic modal mineralogy of different mantle rocks. Pressure increases from left to right.

tectonically exhumed mantle slices (orogenic peridotites, ophiolites, and abyssal peridotites) and lithospheric mantle xenoliths incorporated in volcanic rocks erupted on the Earth's surface. Such mantle xenoliths are common in certain alkali-rich mafic magmas and kimberlites. Field evidence suggests that the upper mantle is peridotitic in composition, although significant heterogeneities are clearly recognized.

From mantle xenoliths, we know that at least the lithospheric mantle underneath continents consists of a variety of peridotite rocks, ranging from dunite to lherzolite, and some eclogite and pyroxenite. The mineralogical composition of these peridotite rocks is dominated by olivine, with much less orthopyroxene, and minor clinopyroxene, and an additional aluminous phase such as plagioclase, spinel, or garnet. **Figure 1(a)** shows the nomenclature of peridotite based on its mineralogical composition (Streckeisen, 1974).

The observed variability in mantle rocks may be described in terms of modal abundances of olivine, orthopyroxene, and clinopyroxene (**Figure 1(a)**) with compositions ranging from fertile Ca- and Al-rich lherzolite to ultradepleted Mg-rich and Ca- and Al-poor dunite (e.g., Carlson et al., 2005). Among these mantle rocks, lherzolites dominate in orogenic peridotites massifs, while harzburgites and dunites predominate in ophiolites and abyssal peridotites. Most mantle xenoliths are reported in volcanic rocks found on continents and xenoliths from the oceanic mantle are rare. Only few samples have been reported from the Azores, Hawaii, and the Canary Islands (e.g., Coltorti et al., 2010; Merle et al., 2012; Yamamoto et al., 2009), which probably represent the thicker lithosphere beneath ocean islands. Alkali basalt usually contains xenoliths ranging from spinel lherzolite, spinel harzburgite, to spinel-bearing dunite. Garnet-bearing xenoliths are only rarely sampled by basalts (e.g., Bjerg et al., 2009; Goncharov and Ionov, 2012; Harris et al., 2010). Xenoliths from kimberlites, which sample the lithosphere beneath much thicker cratonic lithosphere, range from fertile garnet-bearing lherzolites to depleted harzburgites and dunites, and spinel-bearing peridotites as well. As kimberlites and lamproites sometimes contain diamonds, the

study of diamond inclusions frequently shows that olivine, garnet, spinel, pyroxene, and, sometimes, other less common phases such as sulfides or exotic oxides occur as inclusions in diamond (Bulanova et al., 2004; Haggerty et al., 1989; Nixon and Condcliffe, 1989; Stachel and Harris, 2008).

We will not attempt to review all the available geochemical data that explain the chemical variability of bulk upper mantle, but the interested reader is referred to the excellent review of Bodinier and Godard (2003) on orogenic and abyssal mantle rock geochemistry and to Pearson et al. (2003) on mantle xenoliths. We will instead briefly refer to the main processes that are known to cause heterogeneities in the upper mantle. There are two main processes that are known to cause heterogeneity in mantle rocks. Firstly, melt extraction from a peridotite mantle rock explains a large proportion of depleted or enriched bulk compositions recognized in tectonically emplaced peridotites as well as mantle xenoliths (e.g., Walter et al., 2004). Secondly, the interaction, at different scales and depths, of ascending melts with adjacent mantle rocks is recognized to cause further chemical variation of mantle rocks (e.g., Kelemen et al., 1997).

From experimental information, we know that partial melting of lherzolite (some 10–30%) leads to ordinary basaltic melts, which, due to a much lower density than the mantle rocks, rise from the mantle into the crust. During partial melting, incompatible elements (such as Na, K, Ca, and Al) preferentially partition into the melt and compatible elements (such as Mg) preferentially stay behind in the residual mantle. Thus, melting of the mantle rocks causes chemical differentiation, which depletes the residual mantle rocks in incompatible elements. Lherzolites therefore represent a fertile bulk composition able to produce basaltic magmas by partial melting, while harzburgites or dunites represent the most depleted mantle bulk composition with poor efficiency to produce mafic partial melts. The melting process of the peridotite rock is complex (Ghiorso and Sack, 1995; Ghiorso et al., 2002; Presnall et al., 2002; Walter, 1998) and involves all mantle minerals albeit clinopyroxene and also garnet are most affected by melting.

This implies that the small amount of clinopyroxene present in lherzolites will completely disappear during higher degrees of partial melting. During even higher degrees of partial melting (or further reaction of mantle rock with melts), other minerals such as orthopyroxene are also significantly affected by melting, leaving behind an even more depleted mantle peridotite such as harzburgite or even dunite.

From a geochemical point of view, variations of bulk composition within the mantle are conveniently represented by covariance diagrams that use major elements to illustrate magmatic processes. Al_2O_3 represents a good chemical marker of depletion, as it is not strongly affected by alteration or serpentinization processes and, when compared with MgO or modal olivine, reveals a large variability both in tectonically exhumed peridotites and in xenoliths (Figure 2). Most natural mantle rocks that plot on such element covariant trends also show similar variations in the X_{Mg} ($X_{\text{Mg}} = \text{Mg}/(\text{Mg} + \text{Fe})$), and the resulting mineral modal proportions are consistent with variable degree of melt extraction during partial melting of asthenospheric mantle (Frey et al., 1985; Jagoutz et al., 1979; McDonough and Frey, 1989; McDonough and Sun, 1995; Ringwood, 1975).

Evidence for a second source of mantle heterogeneity, caused by reactive porous flow melt percolation and melt-rock interaction, has been observed in both orogenic and abyssal peridotites. Marked FeO enrichment and SiO_2 depletion at increasing MgO, and contrasting bulk versus mineral chemistry (e.g., a constant bulk X_{Mg} combined with an increase of modal olivine with constant forsterite content), reported both in natural samples (Niu et al., 1997; Rampone et al., 2004) and in experimental charges (Lambart et al., 2009) rule out that mantle differentiation occurs only by partial melting and clearly supports the melt-rock reaction processes.

Summarizing, it is now widely accepted that both partial melting processes and melt-rock interaction processes operate

at different levels within the mantle. Depending on the melt composition, the depth at which the interaction occurs, and the thermal contrast between melts and solid rocks, different lithologies develop, which accounts for a large range of the observed mantle compositions. Dissolution of orthopyroxene and precipitation of olivine by porous flow produce 'replacive dunites' and 'reactive harzburgites,' with bulk chemical and modal depletion and peculiar structural-textural features documented in an increasing number of studies of both 'on land' peridotites and abyssal mantle rocks (Godard et al., 2000; Kelemen, 1990; Kelemen et al., 1992, 1995a,b, 1997; Niu et al., 1997; Quick, 1981; Rampone et al., 2004; Seyler et al., 2007; Van der Wal and Bodinier, 1996). On the other hand, at shallower levels, melt infiltration and impregnation lead to the formation of refertilized lithologies by interstitial recrystallization of percolating melts. Numerous plagioclase-rich peridotites have been documented in present-day oceanic settings, both in slow-spreading (Cannat et al., 1992; Dick, 1989; Seyler and Bonatti, 1997; Tartarotti et al., 2002) and in fast-spreading ridge/transform systems (Constantin et al., 1995; Hebert et al., 1983; Hekinian et al., 1993), as well as in ophiolites (Boudier and Nicolas, 1977; Dijkstra et al., 2003; Kaczmarek and Müntener, 2010; Nicolas, 1986; Piccardo et al., 2007; Rampone et al., 1997, 2008). These rocks have modified modal distributions and can host a greater amount of plagioclase than usually expected by metamorphic reequilibration within the plagioclase facies during tectonic exhumation of mantle rocks. Such a modal diversity can contribute, if seismically detectable, to different geophysical signals and needs to be taken into account for processes that occur in shallower mantle settings, for example, in extensional regimes.

Heterogeneities have been also recognized in the deeper convective mantle. The considerable body of new trace element and radiogenic isotopic data on basalts and related residual mantle reservoirs have revealed that conventional melt

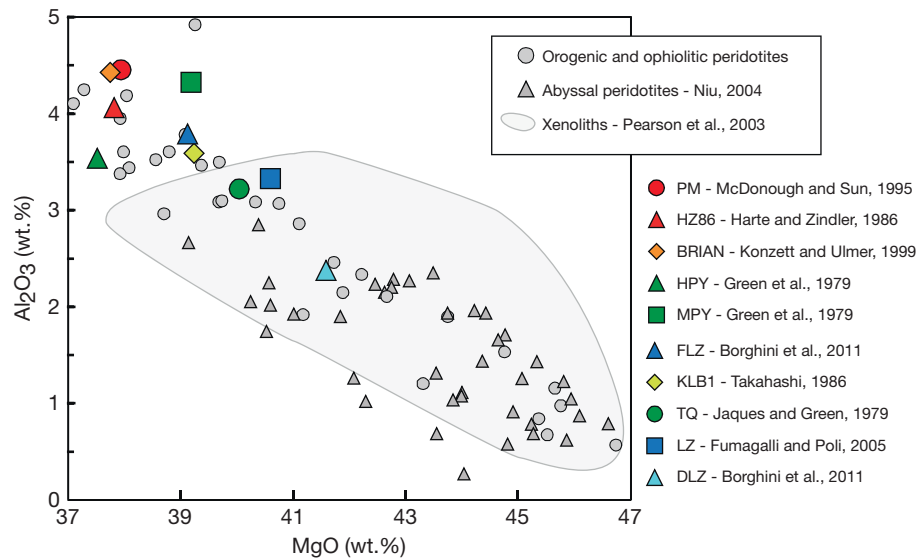


Figure 2 Al_2O_3 (wt.%) versus MgO (wt.%) diagram showing the variety of mantle compositions in orogenic and ophiolitic peridotites (gray circles; data are from Bodinier et al. (1988, 2008), Fabriès et al. (1989, 1998), Lenoir et al. (2001), Le Roux et al. (2007), Rampone et al. (1995, 1996, 2004, 2005), Sinigoi et al. (1980), Van der Wal and Bodinier (1996), and Voshage et al. (1988)), abyssal peridotites (gray triangles; data are from Niu, 1997), and mantle xenoliths (gray shaded area; data are from Pearson et al., 2003) compared with various bulk compositions used in experiments (colored symbols).

extraction processes cannot explain all the observed geochemical signatures (Rampone and Hofmann, 2012; Salters et al., 2011; Stracke et al., 2005; Willbold and Stracke, 2010; Zindler et al., 1984). The latter require chemical differences within the convective mantle, that is, the source of primary basaltic magmas, which implies significant heterogeneities also in the convecting mantle. Over the last decades, many studies addressed processes that may cause heterogeneities in the upper mantle, using both field-based and experimental investigations. Three main causes have been identified in the review paper by Rampone and Hofmann (2012): (i) old depletion events not completely rehomogenized, (ii) the contribution of pyroxenite component in the mantle source (Lambart et al., 2013), and (iii) metasomatism and melt–rock interactions by deep intrusions. Although it is beyond the scope of this review to go into much detail about the rather controversial issues, the role of pyroxenites and metasomatic processes seems worth mentioning. The role of pyroxenites as an additional source in the upper mantle to generate the variable range of mid-ocean ridge basalts (MORBs) and ocean island basalt (OIB) has been extensively investigated over the past two decades both experimentally (e.g., Hirschmann et al., 2003; Klemme et al., 2002; Lambart et al., 2013; Mallik and Dasgupta, 2012; Pertermann and Hirschmann, 2003; Sobolev et al., 2007; Yaxley and Green, 1998) and by geochemical modeling (Kogiso et al., 2004; Stracke and Bourdon, 2009; Stracke et al., 1999). This scientific interest mainly stems from the ubiquity of pyroxenites and mafic eclogites in both mantle xenoliths and ultramafic massifs and also from the chemical variability of oceanic basalts, which is not easily explained by partial melting of peridotite composition alone. Moreover, eclogites are frequently found as xenoliths especially in cratonic environments and make up some 2% on average (Schulze, 1989). In noncratonic xenoliths, pyroxenites and garnet pyroxenites are more common and eclogites are quite rare. Cratonic eclogites are distinguishable from crustal eclogites by the occurrence of diamond, the Na content in garnet, and the K content in clinopyroxenes, all features that are in agreement with a high-pressure origin (Pearson et al., 2003).

A different origin has been proposed for the pyroxenites (Bodinier and Godard, 2003; Downes, 2007). It seems clear that some of them are remnants of old recycled oceanic crust (Allègre and Turcotte, 1986; Blichert-Toft et al., 1999; Morishita et al., 2001; Morishita et al., 2003, 2004; Pearson and Nowell, 2004; Pearson et al., 1993) that was not completely remixed into the mantle, resulting in a veined mantle or ‘marble cake-like’ mantle. These pyroxenite-bearing parts of the mantle are known to melt at lower temperature than peridotites (Klemme et al., 2002; Pertermann and Hirschmann, 2003; Yaxley and Green, 1998). Other pyroxenites are clearly related to melt–rock interactions when the host peridotites were already incorporated at lithospheric environments (Bodinier and Godard, 2003; Bodinier et al., 1987a,b, 1988, 2008; Garrido and Bodinier, 1999; Takazawa et al., 1996). Subsequent interactions among pyroxenites, partial melts, and their host peridotites can account for the genesis of a second generation of pyroxenites, which cause further mantle heterogeneity on a different scale and with a larger compositional range (Lambart et al., 2013).

At convergent plate boundaries, for example, in subduction zones, the recycling of the oceanic crust causes a wide range of

metasomatic reactions. Interactions of different melts or fluids derived from the subducted crust with the overlying mantle rocks create a wide range of different rocks, which commonly contain metasomatic minerals. Phlogopite–spinel peridotites (Nixon, 1987), phlogopite–garnet peridotites, phlogopite–K-richertite peridotite xenoliths, and ‘orogenic’ phlogopite peridotites of ultrahigh-pressure terrains (Bardane peridotite, Norway: van Roermund et al., 2002; Sulu garnet peridotite, China: Zhang et al., 2007; Ulten peridotite: Rampone and Morten, 2001) document efficient mass transfer from the slab toward the mantle wedge and document global chemical recycling processes in subduction zones.

In summary, recent studies have clearly shown that the mineralogical and chemical compositions of the Earth’s mantle are, at least in parts, heterogeneous. However, the scale and the residence time of heterogeneities within a convecting mantle are important factors controlling the petrologic and geochemical evolution of the mantle (Xu et al., 2008). The observed heterogeneities range from cm scale to regional scale, but it is currently not fully understood (i) if the observed heterogeneities are detectable with geophysical methods and (ii) how efficient the dynamic mantle is to rehomogenize such heterogeneities. Both issues need further investigations. In this respect, a pyrolite model for the Earth’s mantle, which assumes a homogeneous mantle, represents one end-member of a range of bulk compositions (Stixrude and Lithgow-Bertelloni, 2012).

In the next paragraphs, we aim to present the effects of variable chemical compositions on the mineralogical composition of the mantle. This will help investigate changes in modal mineral abundances and physical properties with depth. We will focus on experimental methods that are crucial for such endeavors, starting from chemical compositions, which are often chosen as starting material, followed by a brief overview of experimental techniques used and experimental results on important mineral phase transitions and mineral reactions observed in the upper mantle.

2.02.3 Experimental Petrology and the Mineralogical Composition of the Earth’s Upper Mantle

While it is obvious that the mineralogical composition of the mantle must be related to its chemical composition, one must consider the fact that many mantle minerals are complex solid solutions and can, therefore, incorporate several elements and display a more or less wide range of chemical compositions. This implies that small differences in chemical composition of the mantle may not stabilize additional mineral phases but can be accounted for by the rather flexible mineral compositions.

Experimental petrology and geochemistry is fundamentally important in constraining the behavior of Earth materials as a function of pressure, temperature, and bulk composition, providing further constraints on the mineralogical composition of the upper mantle. The main tasks are not only related to the definition of the stability fields of upper mantle phases but also, perhaps more interestingly, related to the way in which mineral assemblages change as a result of changes in several thermodynamic variables. Changes of pressure and temperature will eventually lead to changes not only in crystallographic structure of a mineral or a phase transition, but, in complex

compositions, pressure and temperature variations often result in changing modal abundances of minerals and chemical reactions among minerals. In this context, petrologists distinguish two main kinds of transformations: discontinuous and continuous reactions. Discontinuous reactions imply an abrupt disappearance or appearance of a new phase and are usually represented by comparing chemographies at different pressure and temperature conditions. In contrast, continuous reactions involve continuous changes in phase compositions as a function of pressure or temperature. Continuous reactions usually occur in systems with a large number of chemical components with often extensive solid solutions. This kind of reactions is usually best described by means of divariant (or multivariant) loops in pressure–composition or temperature–composition diagrams.

It should be noted that most experiments relevant to the mantle were undertaken in simplified chemical compositions, which only approximate the complex, that is, multi-component, Earth's mantle. Following [Holloway and Wood \(1988\)](#), there are two general types of experiments, namely, studies in chemically simplified compositions and experiments of individual natural rock compositions. Both approaches are valid and useful.

In simple systems, the bulk composition of the mantle (e.g., pyrolite, [Table 1](#)) is approximated in terms of chemical composition. While it is at the discretion of the experimentalist to choose a particular composition, often, a system is chosen that is simple but contains most (or better, all) relevant mantle phases. A system that fulfills these requirements and consequently one of the most commonly used systems is the system CaO–MgO–Al₂O₃–SiO₂ (CMAS). While experiments in simple systems may not be directly applicable to complex natural compositions, they are useful for thermodynamic interpretation (i.e., extraction of thermodynamic data) or identification of specific mineral reactions as a function of pressure and temperature. Furthermore, quality control of experiments in simple systems is straightforward with the aid of so-called reversal experiments in which the *P–T–X* conditions of equilibrium among different phases are constrained by approaching them from opposing directions. In this context, ‘reversal’ of an experiment means that the attainment of equilibrium between phases is tested by repeated experiments, which approach equilibrium from different (mainly compositional) sides. Having evaluated the experimental results, thermodynamic data for one or more phases may be extracted from the

Table 1 Selected bulk compositions used to model mantle compositions in complex systems

	<i>FLZ</i>	<i>DLZ</i>	<i>PM</i>	<i>LZ</i>	<i>HPY</i>
References	Borghini et al. (2010)	Borghini et al. (2010)	McDonough and Sun (1995)	Fumagalli and Poli (2005)	Green (1973)
SiO ₂	44.90	44.90	45.07	45.75	45.21
TiO ₂	0.12	0.07	0.17	0.00	0.71
Al ₂ O ₃	3.79	2.38	4.45	3.33	3.54
Cr ₂ O ₃	0.41	0.39	0.38	0.00	0.43
FeO*	7.99	8.34	8.08	7.03	8.47
MnO	0.00	0.00	0.00	0.00	0.14
MgO	39.12	41.58	37.94	40.59	37.51
CaO	3.41	2.14	3.55	3.11	3.08
Na ₂ O	0.26	0.20	0.36	0.19	0.57
NiO	0.00	0.00	0.00	0.00	0.20
K ₂ O	0.00	0.00	0.00	0.00	0.13
Tot	100.00	100.00	100.00	100.00	100.00
Mg# bulk	0.90	0.90	0.89	0.91	0.89
XCr bulk	0.07	0.10	0.05	0.00	0.08
Na ₂ O/CaO	0.08	0.09	0.10	0.00	0.19
	<i>MPY</i>	<i>TQ</i>	<i>KLB-1</i>	<i>HZ86</i>	<i>BRIAN</i>
References	Green et al. (1979)	Jaques and Green (1979)	Takahashi (1986)	Hart and Zindler (1986)	Konzett and Ulmer (1999)
SiO ₂	44.30	44.96	44.49	46.03	45.92
TiO ₂	0.17	0.08	0.16	0.18	0
Al ₂ O ₃	4.33	3.22	3.59	4.06	4.43
Cr ₂ O ₃	0.45	0.45	0.31	0.40	0
FeO*	7.48	7.66	8.10	7.56	7.04
MnO	0.11	0.14	0.12	0.10	0.00
MgO	39.18	40.04	39.23	37.82	37.74
CaO	3.35	2.99	3.44	3.22	3.59
Na ₂ O	0.40	0.18	0.30	0.33	0.71
NiO	0.26	0.26	0.25	0.28	0
K ₂ O	0.00	0.02	0.00	0.03	0.57
Tot	100.00	100.00	100.00	100.00	100
Mg# bulk	0.90	0.90	0.90	0.90	0.91
XCr bulk	0.06	0.09	0.05	0.06	–
Na ₂ O/CaO	0.12	0.06	0.09	0.10	0.20

FeO* is total iron; Mg# = Mg/(Mg+Fe); X_{Cr} = Cr/(Cr+Al).

results. This leads to a comprehensive set of thermodynamic data by which, if correct and complete, one would be able to calculate phase relations in complex mantle compositions. Although such calculations are rather comprehensive in crustal compositions (e.g., [Holland and Powell, 1998, 2011](#)), we will show below that the data set is far from complete for mantle compositions. On the other hand, experiments in multi-component systems are chemically very close to natural rocks, but quality control of such experiments is more difficult. Experiments in complex compositions are often crippled by very small crystal sizes, disequilibrium textures and compositions, and poor(er) reproducibility. Furthermore, due to a large number of components and phases, and high degree of freedom, experiments cannot be reversed as easily as in simple systems. This implies that it is not straightforward to assess the attainment of equilibrium between all phases in complex composition experiments. Nevertheless, experiments in natural (or close to natural) compositions are useful in combination with the information derived from simple systems.

In the next paragraphs, we will first summarize the main bulk compositions used in experimental investigations of complex systems, then we will briefly examine the experimental techniques and high-pressure apparatus used, and finally we will examine experimental results on major mineralogical changes in the Earth's upper mantle. In this context, we will try to show the fundamental differences between experimental results in simple versus complex systems, which are close to natural compositions. Furthermore, as computer-based phase equilibrium calculations relevant to the upper mantle are emerging, we will also present some selected results derived from thermodynamic modeling of phase relations in mantle compositions.

2.02.3.1 Upper Mantle Bulk Compositions Used in Experiments

Basalts are direct products of melting processes within the Earth's mantle. Consequently, their compositions may be used to constrain the chemical composition of the Earth's mantle. This rationale led to the development of the so-called 'pyrolite' mantle model by [Ringwood \(1975\)](#). Pyrolite is a composite term derived from 'pyr'oxene and 'oli'vine and represents a peridotite mantle that is olivine and pyroxene-rich, which was calculated from complementary basaltic and depleted peridotite rock compositions ([Green and Falloon, 1998](#)). Since then, numerous experiments were conducted in fertile 'pyrolite' compositions, which have helped to constrain the origin of basalts (e.g., [Clark and Ringwood, 1964](#); [Green and Falloon, 1998](#); [Green and Ringwood, 1967](#); [Irifune, 1994](#); [Ishii et al., 2011](#); [Kesson et al., 1998](#); [Robinson and Wood, 1998](#); [Sanehira et al., 2008](#)). Several other chemical compositions for a fertile mantle have since been proposed, based either on geochemical and cosmochemical constraints (e.g., [Palme and O'Neill, 2003](#)) or on compositions of fertile or other mantle xenoliths (e.g., [Green and Falloon, 1998](#); [Takahashi, 1986](#); [Takahashi et al., 1993](#)). In addition to the experiments in pyrolite-type compositions, numerous experiments have been conducted in chemical compositions based on relatively fertile mantle xenoliths, such as the Kilbourne Hole lherzolite (KLB-1) ([Takahashi, 1986](#); [Takahashi et al.,](#)

[1993](#)) or the Tinaquillo lherzolite ([Jaques and Green, 1980](#); [McDade et al., 2003](#)). Starting materials close to natural compositions were taken from natural occurrences of peridotites such as the fertile lherzolite (FLZ) and depleted lherzolite (DLZ) used to investigate the plagioclase–spinel transition ([Borghini et al., 2011](#)). The effect of potassium, of relevance for the study of metasomatic reactions in subduction zones, was investigated in K-bearing lherzolites (e.g., [Fumagalli et al., 2009](#); [Konzett and Ulmer, 1999](#)).

It is worth noting that, when partial melting occurs, even small differences in incompatible element concentration (such as Na or K) of the source drastically affect the melt composition and physical properties. Subsolvus phase relations, however, are only slightly affected by small chemical differences of the bulk. Nonetheless, additional components certainly enable continuous reactions to occur, and multivariant phase assemblages to be taken into account.

2.02.3.2 Experimental Methods: High-Pressure High-Temperature Apparatus

To constrain the mineralogical composition of the mantle, one needs to identify the effect of pressure, temperature, and chemical composition on phase relations of the upper mantle. To this effect, experiments at high pressure and high temperature were conducted to simulate mineralogical transformations in the laboratory. These experiments began in the early 1950 and 1960s with the development of reliable high-pressure apparatus such as the piston–cylinder apparatus and the multi-anvil apparatus ([Figure 3](#)). While there are numerous high-pressure apparatus available, two kinds of high-pressure apparatus are nowadays commonly employed to simulate the pressure–temperature conditions of the upper mantle in the laboratory. The classical paper by [Boyd and England \(1960\)](#) describes a piston–cylinder apparatus that is capable of routinely generating pressures up to about 4 GPa and temperatures of more than 2000 °C. Hydraulic presses drive a carbide piston through

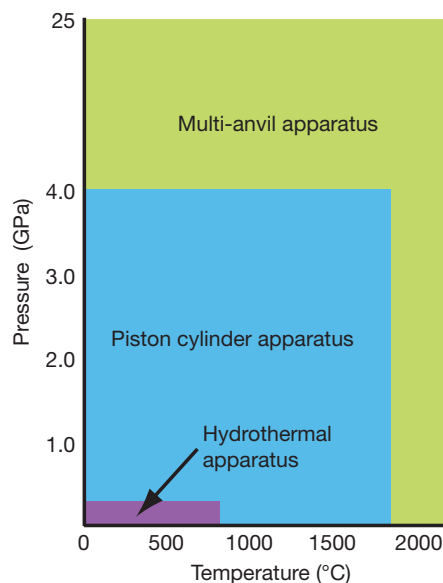


Figure 3 Pressure–temperature range of the main high-pressure apparatus used in experimental petrology.

a large steel-supported carbide cylinder against a top plate to provide a load. Solid-state assemblies are designed to transfer this load onto a sample to generate pressures. Typical sample size is 10–30 mg. Since then, many laboratories have built similar devices that have proven to be reliable, safe to operate, and, compared to other high-pressure apparatus, relatively cost-effective. In Europe alone, there are some 30 laboratories, including our own at Milan and Münster, which employ piston–cylinder apparatus routinely to study high-pressure phase relations, not only in a geological context but also in materials sciences. The pressure range of the piston–cylinder apparatus is limited to about 4 GPa at temperatures up to 2000 °C for routine experimentation. These pressure–temperature conditions correspond to a depth of about 120 km. To investigate deeper parts of the Earth, another apparatus is needed. The high-pressure conditions needed for this kind of work can be generated with a ‘multi-anvil apparatus,’ which is capable of generating pressures of more than 20 GPa at corresponding mantle temperatures. This is more than sufficient to cover the entire range of the upper mantle, which is generally thought to extend to about 400 km depths. Multi-anvil apparatus have been pioneered in the 1950s by H. Tracy Hall who constructed the first tetrahedral apparatus (Hall, 1958). Since then, a number of multi-anvil devices have been constructed and the interested reader is referred to an excellent review paper (Liebermann, 2011).

Most multi-anvil experiments of relevance to the upper mantle require pressures of only up to 15 GPa, and the most reliable and safest apparatus in this context is a modified split-sphere apparatus, the so-called ‘Walker-type’ multi-anvil module (Walker et al., 1990). This Walker-type multi-anvil apparatus is relatively straightforward to use, reliable, and safe. In Europe alone, we counted more than ten laboratories including our own, which routinely employ a Walker-type multi-anvil apparatus to study phase relations in the Earth’s upper mantle. So far, several hundred experimental studies have been conducted to constrain the chemical and mineralogical composition of the upper mantle, and the data set is far from complete, particularly in complex, natural compositions relevant to the upper mantle.

2.02.4 Phase Transitions in Dry Earth’s Upper Mantle

2.02.4.1 The Plagioclase–Spinel Transition

The stability of plagioclase at upper mantle conditions was pioneered in experimental studies (CaO–Al₂O₃–SiO₂: Kushiro and Yoder, 1966; CMAS: Gasparik, 1984; Green and Hibberson, 1970; Herzberg, 1978; Kushiro and Yoder, 1966; MacGregor, 1967; Obata, 1976; O’Hara, 1967) that located the univariant transition in this simple chemical composition between 0.6 and 0.8 GPa, at 900–1200 °C (Figure 4).

More complex systems were investigated subsequently (Na₂O–CMAS: Walter and Presnall, 1994; FeO–CMAS: Gudfinnsson and Presnall, 2000), and although these studies were primarily aimed to locate the solidus temperature of peridotites (e.g., Baker and Stolper, 1994; Baker et al., 1995; Falloon and Green, 1987, 1988; Falloon et al., 1997, 1999; Gudfinnsson and Presnall, 2000; Jaques and Green, 1980; Takahashi, 1986; Walter and Presnall, 1994), the investigators recognized a divariant field, which is characterized by the

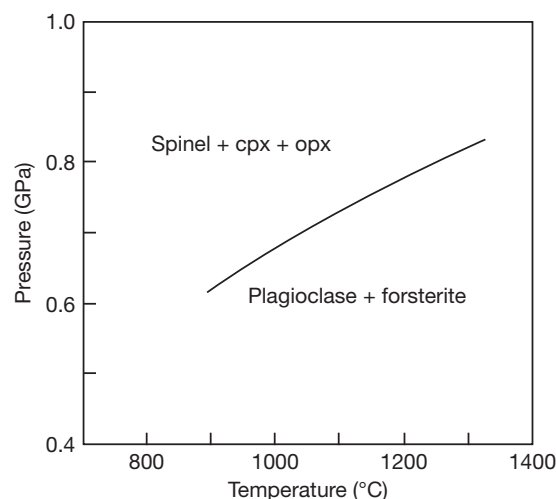


Figure 4 The plagioclase–spinel transition in the system CaO–MgO–Al₂O₃–SiO₂. References are given in the text.

coexistence of plagioclase and spinel and demonstrates the continuous nature of the plagioclase–spinel transition (Green and Falloon, 1998; Green and Hibberson, 1970; Gudfinnsson and Presnall, 2000; Presnall et al., 2002; Walter and Presnall, 1994). More recently, subsolidus experiments in the complex system TiO₂–Cr₂O₃–Na₂O–FeO–CMAS quantitatively constrained the effect of different bulk compositions on the location of the reaction and described subsolidus mineral compositional variations as a result of Na and Ca partitioning between plagioclase and clinopyroxene and of Cr, Al partitioning between pyroxenes and spinel (Borghini et al., 2010). In particular, the location of the transition is described in terms of two chemical bulk parameters: the bulk Na/Ca ratio and the bulk X_{Cr} (X_{Cr} = Cr/(Cr + Al) that describes the degree of depletion of the mantle rock. While higher Na in the bulk composition increases plagioclase stability, consequently shifting the transition toward higher pressure, increasing Cr in the bulk composition decreases plagioclase stability relative to spinel. As a result, bulk compositions with higher Cr spinel/anorthite normative ratios would result in Cr-rich spinels and a plagioclase-out boundary at progressively lower pressures. The available experimental data in complex systems confirm this trend (Figure 5).

The experimentally derived data are also confirmed by naturally occurring mantle rocks (Figure 1(b)). Most shallow mantle xenoliths contain both spinel and plagioclase (Sen, 1988; Zipfel and Woner, 1992). Field-based studies on plagioclase peridotites from orogenic massifs (Furusho and Kanagawa, 1999; Newman et al., 1999; Ozawa and Takahashi, 1995) documented a systematic increase of anorthite from core to rim of single plagioclase crystals (referred to as ‘reverse zoning’) and interpreted this as the result of a continuous subsolidus reaction between two pyroxenes and spinel driven by progressive decompression and uplift of the peridotites (Newman et al., 1999; Ozawa and Takahashi, 1995).

One of the major applications of such experimental results is related to the fact that they allow estimation of the pressure history that peridotites underwent during their uplift at extensional settings. This allows reconstructions of the exhumation

history of lithospheric upper mantle as shown recently by [Borghini et al. \(2011\)](#). However, the observed changes in mineral chemistry of all coexisting phases within the plagioclase stability field, and the continuous nature of the transition, additionally suggest that, as a result of mass balance condition, the modal proportions of minerals need to change as well. [Borghini et al. \(2010\)](#) have quantitatively examined the progressive decrease of modal plagioclase with increasing pressure up to the plagioclase-out boundary in fertile and depleted bulk composition. They find that modal plagioclase abundances varied between 8.8 and 4.8 wt.% at 0.3–0.8 GPa in a FLZ composition and between 5 and 3.2 wt.% at about 0.3–0.7 GPa in DLZs. These modal abundances are more than 60% lower than the amounts of plagioclase predicted by simple thermodynamic models that are commonly adopted in modeling phase equilibria of the uppermost lithospheric mantle (e.g., [Simon and Podladchikov, 2008](#); [Wood and Yuen, 1983](#)). On the other hand, it should also be noted that the modal plagioclase found in the experiments probably represents an overestimation with respect to natural occurrences, where low-pressure recrystallization is generally confined to discrete microstructural domains between spinel-facies porphyroclastic minerals ([Cannat and Seyler, 1995](#); [Fabries et al., 1998](#); [Hoogerduijn Strating et al., 1993](#); [Montanini et al., 2006](#); [Newman et al., 1999](#); [Obata, 1980](#); [Ozawa and Takahashi, 1995](#); [Rampone et al., 1993, 1995, 2005](#); [Takazawa et al., 1996](#)). On the other hand, higher plagioclase

abundances are expected in natural peridotites, which are re-fertilized by melt–rock reactions. In these cases, the modal abundance of plagioclase would be underestimated leading to the underestimation of the effect of plagioclase modes on the density profile and seismic properties of these rocks.

2.02.4.2 The Spinel–Garnet Transition

The transition from spinel peridotite to garnet-bearing peridotite (either FLZ or depleted harzburgite) is one of the most important phase boundaries in the upper mantle. We know from the xenolith information that spinel lherzolite xenoliths are common in alkaline volcanics and there are only a few localities worldwide where garnet-bearing xenoliths are found. Kimberlites, however, contain both spinel peridotite and garnet peridotite xenoliths, occasionally also garnet- and spinel-bearing samples (e.g., [Canil and O'Neill, 1996](#); [Ganguly and Bhattacharya, 1987](#); [Ionov et al., 1993](#)). The transition from spinel to garnet in the Earth's upper mantle has been studied experimentally in a variety of simple systems as well as in natural compositions, although more and better data are needed for the latter.

We begin with the simplest chemical composition, which contains all relevant mantle phases. This is the system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ (MAS) and the system CMAS. Both simple systems contain olivine (Mg_2SiO_4 – forsterite), Al-bearing orthopyroxene, Al-bearing clinopyroxene, spinel (MgAl_2O_4), and garnet ($(\text{Ca,Mg})_3\text{Al}_2\text{Si}_3\text{O}_{12}$). These systems were studied a number of times ([Brey et al., 1986](#); [Danckwerts and Newton, 1978](#); [Gasparik and Newton, 1984](#); [Herzberg, 1978](#); [Klemme and O'Neill, 2000](#); [Lane and Ganguly, 1980](#); [MacGregor, 1974](#); [Nickel et al., 1985](#); [O'Hara et al., 1971](#); [O'Neill, 1981](#); [Obata, 1976](#); [Perkins and Newton, 1980](#)), and it was shown that the spinel–garnet transition is univariant (i.e., a line in a pressure–temperature diagram) in this system.

In conclusion, phase relations in simple systems, such as CMAS and MAS, are useful in constraining phase relations of the upper mantle. [Figure 6](#) shows the garnet–spinel and the plagioclase–spinel transitions in CMAS, based on the most

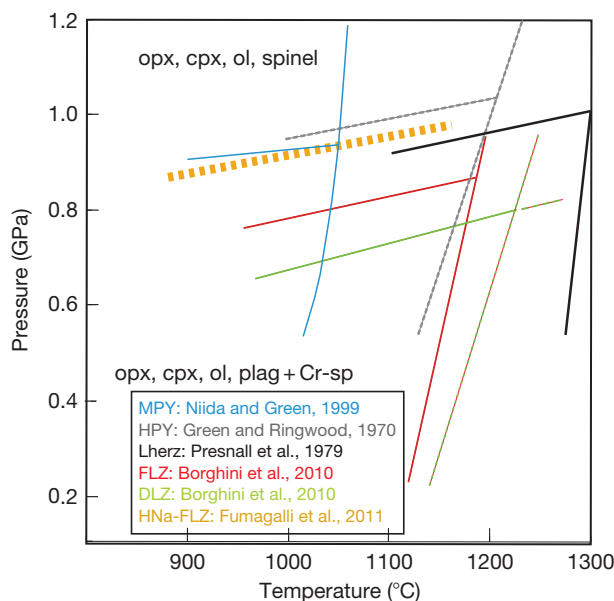


Figure 5 The plagioclase–spinel transition in complex compositions: pale blue: MORB Pyrolite (MPY), [Niida and Green \(1999\)](#); stippled gray: Hawaiian Pyrolite - HPY, [Green and Ringwood \(1970\)](#); black: Lherzolite in the $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ system (Lherz) [Presnall et al. \(1979\)](#); red: Fertile Lherzolite (FLZ), [Borghini et al. \(2010\)](#); apple green: Depleted Lherzolite (DLZ), [Borghini et al. \(2010\)](#); stippled ocker: High Na Fertile Lherzolite (HNa-FLZ), [Fumagalli et al. \(2011\)](#). Different bulk compositions differ in the Na/Ca bulk ratio and bulk X_{Cr} ($X_{\text{Cr}} = \text{Cr}/(\text{Cr} + \text{Al})$): [Presnall et al. \(1979\)](#) investigated Cr-free system, with the lowest bulk $\text{Na}_2\text{O}/\text{CaO}$ ratio. FLZ, HNa-FLZ, MPY, and HPY have similar bulk X_{Cr} but increasing values of $\text{Na}_2\text{O}/\text{CaO}$ ratio. Depleted Lherzolite has the same $\text{Na}_2\text{O}/\text{CaO}$ ratio of FLZ, but higher X_{Cr} .

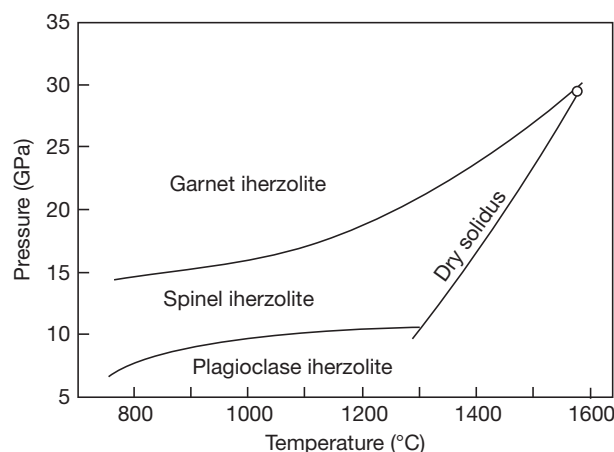


Figure 6 The transition from garnet to spinel lherzolite in the system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ (CMAS). Shown here are phase stability fields based on [O'Neill \(1981\)](#), [Klemme and O'Neill \(2000\)](#), and [Milholland and Presnall \(1998\)](#). See text for details.

recent and most consistent data set (Borghini et al., 2010; Klemme and O'Neill, 2000; Milholland and Presnall, 1998; O'Neill, 1981). The rather steep slope of the high-temperature part of the transition was confirmed recently (Walter et al., 2002). Note that the data displayed here disagree with an older set of experiments (Gasparik, 1984). This may seem insignificant here, but as the Gasparik experiments were used to calibrate the thermodynamic model employed by Holland and Powell (1998, 2011), thermodynamic calculations with the thermocalc model (Holland and Powell, 1998, 2011) are expected to yield unreliable results in mantle compositions involving spinels and garnets (Green et al., 2012).

In more complex chemical compositions, the transition from spinel to garnet-bearing peridotite will have higher degrees of freedom. This implies that the line that separates the spinel from the garnet stability field in Figure 6 will be replaced with a phase stability field in which spinel and garnet coexist. The same will apply to the plagioclase to spinel transition. This also implies that in complex, multicomponent natural compositions, there must be a field in a P - T diagram where spinel and garnet (and plagioclase and spinel) coexist. This explains the coexistence of spinel and garnet in some kimberlites. O'Neill (1981) was one of the first to suggest that Cr^{3+} stabilizes spinel relative to garnet. Addition of Cr to the CMAS system will, therefore, result in a shift of the garnet-in reaction to higher pressures. Similarly, O'Neill (1981) noted that addition of Fe^{2+} to the system will result in a shift of the garnet-in reaction to lower pressures. Since then, further experiments (Brey et al., 1999; Giris and Brey, 1999; Giris et al., 2003; Irifune et al., 1982; Nickel, 1986; Webb and Wood, 1986) and thermodynamic calculations (Ganguly and Bhattacharya, 1987) have confirmed this trend. Recently, it was shown (Klemme, 2004) that in extremely depleted compositions, the garnet-spinel transition occurs at very high

pressure and exhibits a negative Clapeyron slope. Note that these experiments were conducted in a model system ($\text{MgO-Cr}_2\text{O}_3\text{-SiO}_2$) and that these composition are not directly relevant to the mantle, which contains always much more Al than Cr with $\text{Cr}/(\text{Cr}+\text{Al}) < 0.3$ in even the most depleted peridotite. These experiments, however, define the maximum stability of spinel in the mantle and are important in constraining the thermodynamic properties of Cr-rich garnets (Klemme, 2004). Figure 7 shows both the effect of Cr on spinel stability (Figure 7(a)) and the stability of Cr-rich spinel in extremely depleted compositions (Figure 7(b)).

Very little experimental work on the stability of garnet and spinel has been done in complex systems with near-natural compositions. The pioneering experiments of Green and Ringwood (1967) show that there is a narrow garnet plus spinel stability field, which could not be resolved any further using their experimental and analytic techniques. Additional information on the garnet-spinel transition in complex compositions can be derived from experimental studies performed on the stability of pargasite (Niida and Green, 1999) or in peridotite systems (Fumagalli and Poli, 2005; Fumagalli and Stixrude, 2007). Note, however, that, due to slow reaction rates, experiments in natural complex compositions are extremely difficult.

2.02.4.2.1 Phase equilibrium calculations: implications for the Hales discontinuity

More promising perhaps, phase equilibrium calculations in fertile and depleted mantle compositions have recently emerged due to the fact that new thermodynamic data for important mantle minerals have been measured (see Klemme et al., 2009 and Ziberna et al., 2013, for discussion). With some limitations, it has been shown that in natural fertile compositions, the garnet plus spinel stability field is narrow

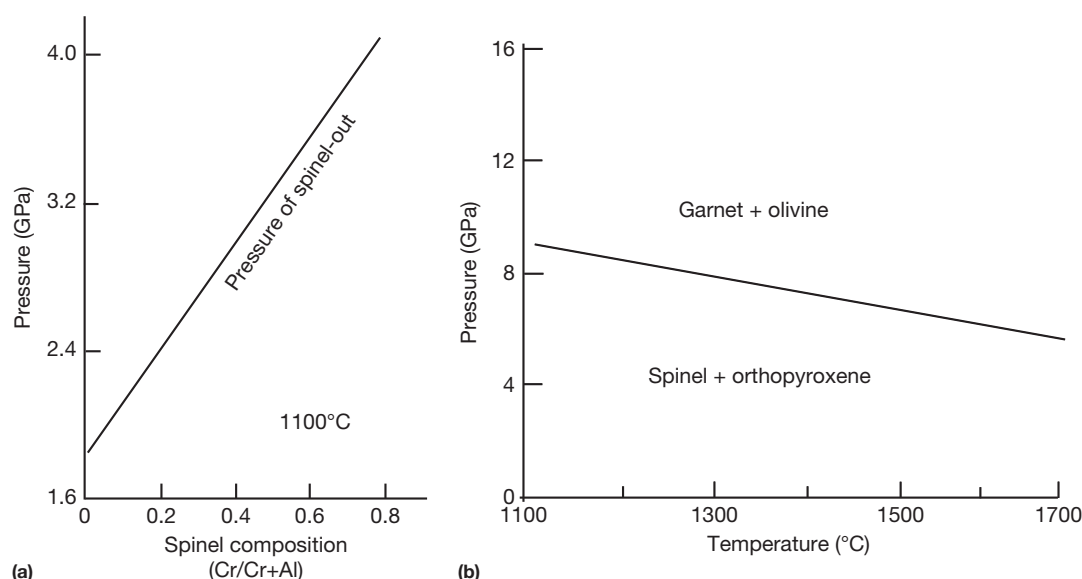


Figure 7 (a) The effect of Cr on the stability of spinel in the mantle in the system CMAS + Cr (Redrawn from O'Neill HSC (1981) The transition between spinel lherzolite and garnet lherzolite, and its use as a geobarometer. *Contributions to Mineralogy and Petrology* 77: 185–194.). (b) The maximum stability of spinel in the mantle (Redrawn from Klemme S (2004) The influence of Cr on the garnet-spinel transition in the Earth's mantle: experiments in the system $\text{MgO-Cr}_2\text{O}_3\text{-SiO}_2$ and thermodynamic modelling. *Lithos* 77: 639–646.).

at high temperatures close to the solidus, but it is very wide at lower temperatures. Ziberna et al. (2013) showed in multi-component, near-natural bulk compositions that the effect of depletion is large in subsolidus phase relations and that Cr-rich spinel can be stable in cold and depleted lithosphere up to pressures of 6 GPa (which corresponds to about 180 km depths). The implications of these results are compelling: the spinel–garnet transition in fertile and hot mantle (e.g., under mid-ocean ridges) should be relatively narrow and should show up in seismological studies as a discontinuity (Hales, 1969). However, assuming that cratonic lithosphere is much colder and also more depleted than ordinary lithosphere, the garnet–spinel transition should be much broader in cratonic regions and only a gradient zone should be observed. Thus, in continental regions with relatively hot geotherms, such as the Variscan orogen in the SW Iberian Peninsula (Palomeras et al., 2011), the Hales gradient zone is only 10–20 km thick and lies at around 70 km depth (Ayarza et al., 2010). In cratonic blocks with colder geotherms, it appears at greater depths and over broader intervals, that is, from the Moho to 150 km depth (Lebedev et al., 2009). Ziberna et al. (2013) further predict that bulk composition may control the extension of the Hales gradient zone in cold, cratonic settings, but its influence will progressively decrease at higher increasing geothermal gradients. Note that there are alternative interpretations of the Hales discontinuity, ranging from seismic anisotropy (Bostock, 1998; Fuchs, 1983; Levin and Park, 2000) to pervasive partial melts (Thybo and Perchuc, 1997) and cation ordering in mantle olivine (Mandal et al., 2012).

2.02.4.3 Garnet–Majorite Reactions

Majorite is a phase in the mantle that is related to garnet. Majorite is named after Alan Major, who synthesized this particular type of garnet at pressures of more than 6 GPa at the Australian National University in the late 1960s (Ringwood and Major, 1971). Compared to normal garnets with a chemical formula of $A_3B_2Si_3O_{12}$, majorite contains excess Si. This is reflected in the general chemical formula for majorite garnets $A_3B_{2-x}Si_{3+x}O_{12}$. The excess Si in majoritic garnets is possible to the fact that high-pressure silicates (all of them) will at some stage incorporate some of its Si not only into the normal tetrahedral site but also into an octahedral site. With increasing pressures, garnets incorporate more and more sixfold coordinated Si due to a continuous reaction with pyroxenes. This was first shown for garnets in experimental charges (Ringwood and Major, 1971), but other silicates show similar effects (e.g., Angel et al., 1988). Note that majoritic garnets are commonly found as inclusions in diamond, but majoritic garnets have been also described in the orogenic garnet peridotite in the Western Gneiss Region of Norway (e.g., Scambelluri et al., 2008; van Roermund et al., 2001). Figure 8 shows the majorite-forming reaction studied in the simple MAS system (Akaogi and Akimoto, 1977). There are very few experiments on the stability of majorite in more complex compositions; one of the few is a study in pyrolite composition (Akaogi and Akimoto, 1979; Irifune, 1987). The experimental data show that the majorite component in the upper mantle garnets (i.e., at depth less than 410 km) is only very small and does not exceed a few percent. Within the transition zone, however,

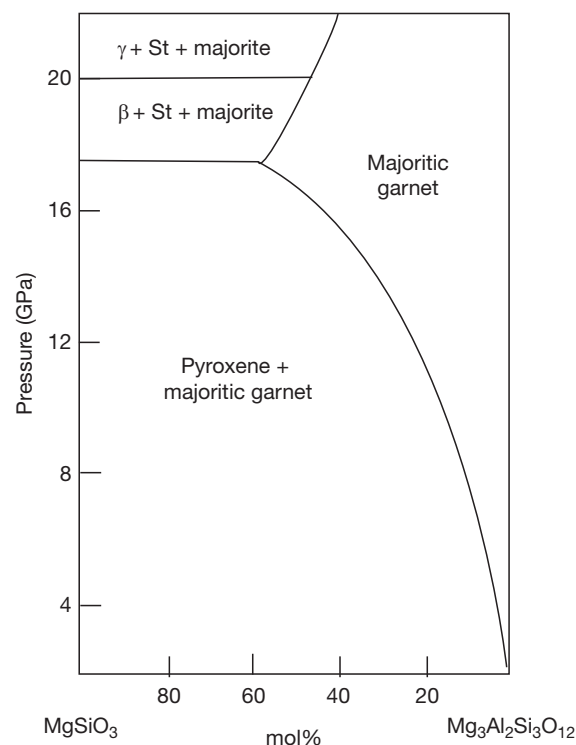


Figure 8 Phase relations in the system $MgO-Al_2O_3-SiO_2$ depicting the formation of majorite garnets, which are a product of increasing solution of pyroxene into the garnet structure. See text for details. Redrawn from Akaogi M and Akimoto S (1977) Pyroxene–garnet solid-solution equilibria in systems $Mg_4Si_4O_{12}-Mg_3Al_2Si_3O_{12}$ and $Fe_4Si_4O_{12}-Fe_3Al_2Si_3O_{12}$ at high-pressures and temperatures. *Physics of the Earth and Planetary Interiors* 15: 90–106.

things change, and garnets are able to dissolve more and more pyroxene components (Figure 8) so that deeper parts of the transition zone are expected to be very rich in majoritic garnets (e.g., Ganguly et al., 2009; Stixrude and Lithgow-Bertelloni, 2011). This, however, is beyond the scope of this chapter.

2.02.5 Mineralogy and Transitions in the Upper Mantle at Subduction Zones

2.02.5.1 The Role of Hydrous Phases

The upper mantle at subduction zones is unusual due to processes that occur during subduction of mafic and other crustal rocks back into the mantle. This is probably the main cause of heterogeneity in the mantle. Furthermore, geophysical observations, the evidence from subduction zone volcanoes, and the study of erupted magmas all suggest that subduction processes are associated with the presence of significant amounts of volatiles, mainly H_2O , CO_2 , S, and halogens. Current estimates of ‘normal’ mantle water content based on cosmochemical and geochemical arguments suggest that the bulk silicate earth contains between 500 and 1900 ppm of water (Jambon and Zimmermann, 1990). However, water is unevenly distributed: the mantle source of MORBs is expected to contain

80–330 ppm of water, the source of OIBs from 200 to 950 ppm (Bolfan-Casanova, 2005; Hirschmann et al., 2005). The evidence from mantle xenoliths suggests that the continental upper mantle water content is around 28–175 ppm (Bell and Rossman, 1992). In contrast, however, island arc magmas suggest that upper mantle at subduction zones may contain up to 1900 ppm water, in agreement with the surficial explosive volcanism and intense seismicity observed in subduction zones. While in oceanic and continental mantle, the water can be solely stored in nominally anhydrous minerals (NAMs) such as olivine and pyroxenes, at convergent margins, additional hydrous phases and/or free water-rich fluids should be present at subsolidus conditions. Phase relations in hydrous ultramafic compositions are important to understand mantle mineralogy and phase transformations at subduction zones.

Water has profound effects on most processes within the Earth's mantle. Phase equilibria are strongly influenced: the melting temperature of mantle rocks is lowered and phase transitions are displaced; water also weakens rocks and minerals, reduces the viscosity of mantle materials, affects the electrical conductivity of mantle rocks, and influences the seismic properties. Geophysical observations of convergent margins report subducting slabs seismically faster than the surrounding. These high-velocity zones are often marked by double seismic zones (DSZs) (Hasegawa et al., 1978): while the upper seismic plane is attributed to the interface between the slab and the overlying mantle wedge, the lower seismic plane is often explained by lithologic heterogeneity within the slab, likely related to the ultramafic portion of the slab (Brudzinski et al., 2007; Peacock, 2001; Yamasaki and Seno, 2003). The reason why these parts of the mantle are the regions where deep seismicity is recorded is often due to the embrittlement caused by dehydration of hydrated mantle minerals.

Experimental investigations into these matters offer the possibility to explore the release of fluids as a function of pressure and temperature, and combining this information with the thermal structure of subduction zones, one can investigate phase transformations within the slab.

In the following paragraphs, emphasis will be given to accessory hydrous phases, which may be (and have been shown to be) stable in the Earth's upper mantle. These minerals document the transport and release of H_2O during subduction, a process that has recently interested many petrologists, geochemists, and geophysicists.

Before going into the detail of some experimentally derived phase diagrams, a few general petrologic considerations should

be taken into account. The storage and release of water within or into the mantle and each flux are closely related to stability of hydrate minerals. Discontinuous reactions are of particular interest when they involve hydrates. The breakdown of hydrous phases will (in most cases) release fluids and therefore cause an abrupt change in the physical properties of the rock, which may be related to geophysical observations. On the other hand, the release of a free fluid phase from such a reaction may not always happen, as under some circumstances hydrates react away in the so-called fluid-conservative reactions. The triangular plots in Figure 9 represent chemographies that are useful to predict the stable phase assemblage at fixed pressure and temperature conditions as a function of variable bulk compositions. The simple system $MgO-SiO_2-H_2O$ (MSH) may be taken as a reference. At P_0, T_0 , a model hydrous peridotite (red circle) contains forsterite, talc, and enstatite. No fluid is present and the line brucite–talc–quartz defines the fluid (i.e., water) saturation condition: bulk compositions falling above will include a fluid phase and rocks below will not include a free fluid but may contain hydrous phase assemblages. This implies that the presence of hydrous phases is not precluded at fluid-absent conditions and – very similar to silicates that might be stable in SiO_2 -undersaturated rocks – hydrates can be stable in H_2O -undersaturated compositions. At P_1, T_1 , the phase assemblage consists of antigorite, forsterite, and enstatite. This is, again, a fluid-absent phase assemblage, and water has been simply transferred from talc to antigorite, without a free fluid phase ever being present. These so-called *discontinuous* reactions are water-conservative and, in the overall picture of transport and release of fluids, are of particular relevance. At P_2, T_2 finally, antigorite breaks down and the peridotite now includes forsterite, enstatite, and a water-rich fluid (Figure 9). Water has been released by the dehydration of antigorite, H_2O saturation has been reached, and a pulse of fluid released from this reaction is expected at the corresponding depth in the mantle. As a result, fluid-present conditions can be achieved by dehydration reactions involving phase assemblages stable at fluid-absent conditions. In complex systems, *continuous* reactions are likely to occur. When continuous reactions involve hydrous phases, the fluid production is continuously decreasing as the reaction proceeds and fluid release is spread over a range of pressure and/or temperature.

As we have seen, breakdown of a hydrated mineral may cause a fluid to be released, with significant consequences such as partial melting of the rock or changing rheological and physical properties of the rock due to the presence of a free

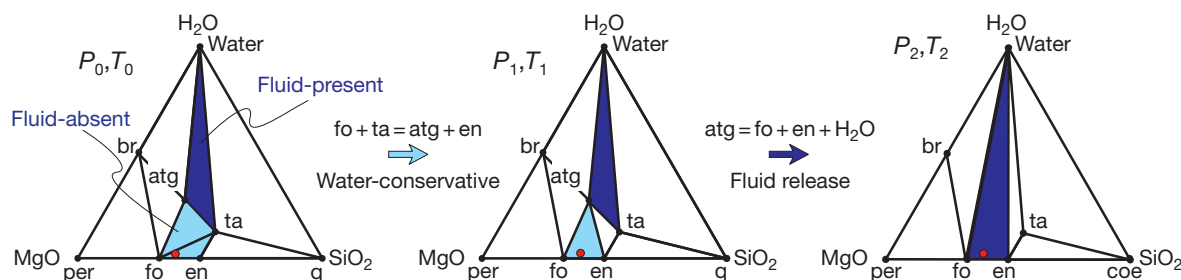


Figure 9 The role of hydrates in the transport and release of fluids at depth is represented in the $MgO-SiO_2-H_2O$ diagrams at different pressure and temperature conditions. The red circle represents a typical simplified peridotite bulk composition. See text for details.

fluid phase. If the fluid production rate is comparable to or higher than viscous relaxation, then embrittlement is expected (Hilairet and Reynard, 2009). In contrast, the breakdown of a hydrated mineral in the upper mantle may involve a complete transfer of the H₂O component into another hydrated mineral via H₂O-conserving reactions. These reactions do not release fluid, but the H₂O component is transferred into other minerals with higher-pressure and/or higher-temperature stability. Investigating the stability, the crystal chemical behavior, and the thermodynamic properties of hydrous phases will further our understanding of how the volatile elements are stored, transferred, or released within the mantle.

Investigations on fast, slow, and ultraslow-spreading ridges suggest different structures of the oceanic crust, with the gabbroic portion less relevant, wider portion of serpentinites and mantle rocks in the latter ones as compared with the original Penrose model, where gabbros constitute the major forming blocks and a layered sequence with mantle rocks confined at the deepest levels (Dick et al., 2012). Prior to subduction, the oceanic crust is altered by hydrothermal processes at the ocean floor (Snow and Dick, 1995) and further hydrated at the outer rise inflections (Contreras-Reyes et al., 2011; Ivandic et al., 2010; Ranero and Sallares, 2004; Ranero et al., 2003). As a result, the input in a subduction zone, that is, the oceanic lithosphere, might be quite heterogeneous as a function of spreading rates and degree and depth of hydration. During subduction, relevant changes in physical properties, first of all density, are accompanied by relevant mineralogical variations, and the role of hydrous phases has been the focus of many studies over the last decades.

In the following parts of our chapter, we will first briefly present experimental constraints on phase relations in mafic lithologies in subducting slabs, and then we will discuss the phase relations in hydrous peridotites, concluding with results on metasomatized lherzolites, which are thought to have formed in subduction zones as a result of interactions between fluids derived from the slab and mantle wedge peridotites.

2.02.5.2 The Basalt to Eclogite Transition

The contribution of the mafic, basaltic, and gabbroic, part of the slab to the transport and release of fluids during subduction, has been extensively investigated both at H₂O-saturated conditions, that is, in the presence of water (Forneris and Holloway, 2003; Litasov and Ohtani, 2005; Okamoto and Maruyama, 2004; Pawley and Holloway, 1993; Poli, 1993; Poli and Schmidt, 1995; Schmidt and Poli, 1998), in the presence of a CO₂ fluid (Molina and Poli, 2000; Yaxley and Green, 1994), and with variable C–O–H fluids (Poli et al., 2009). Besides slight discrepancies, mainly related to different experimental setup and starting materials, all experimental studies suggest that phase relations in mafic systems are dominated by solid solutions and complex continuous reactions, with significant changes in mineral chemistry with *P* and *T* and phase abundances rather than changing phase assemblages. As a result, the bulk composition exerts a fundamental role on phase stabilities, and therefore, experiments performed in certain tholeiitic compositions cannot be simply extrapolated to the wide range of compositions known to exist in basaltic oceanic crust. Furthermore, dehydration reactions occur over a considerable range of

depths and as a consequence the fluid release is expected to be continuously distributed along the slab (e.g., Bose and Ganguly, 1995; Schmidt and Poli, 1998).

At blueschist facies conditions (i.e., deeper than ~15 km), basalts are transformed into rock composed of chlorite, amphibole, phengite, lawsonite or zoisite, and paragonite. At these conditions, the H₂O content of the rock was estimated to be around 6 wt.% (Schmidt and Poli, 2014). The hydrated oceanic crust loses up to two-third of the entire water content before the breakdown of amphibole through numerous dehydration reactions. Amphibole, however, dominates the region where high dehydration rates and fluid production are expected (Schmidt and Poli, 2014). This is why numerous experimental studies have been performed to establish the stability field of amphibole in H₂O-saturated MORB both in simplified chemical compositions (Poli, 1993; Poli and Schmidt, 1995; Schmidt and Poli, 1998) and with natural starting materials (Forneris and Holloway, 2003; Liu et al., 1996; Pawley and Holloway, 1993). Available data (Figure 10) report that at 700–750 °C, amphibole is stable up to a pressure of about 2.5 GPa.

At pressures exceeding the stability of amphibole, other hydrates exist that can account for transport of water into greater depth. Lawsonite and zoisite dominate the higher-pressure regime down to more than 200 km depths (Okamoto and Maruyama, 1999; Ono, 1998; Poli and Schmidt, 1998; Schmidt and Poli, 1998), although other minor phases can also be stable, for example, Mg chloritoid, talc, and phengite. The rock type at these depths is eclogite and the total amount of water that mafic eclogites are able to store in subarc regions is ~1.5 wt.% (Schmidt and Poli, 2014). This deeper part of the subduction zone is therefore characterized by a lower dehydration rate and less fluid production.

Minor amounts of K₂O may stabilize phengite that, with its large stability field well beyond the stability of epidote group minerals, controls most of melting relations and geochemical signature of first partial melts (Okamoto and Maruyama, 1999; Schmidt, 1996). The addition of a CO₂ component further complicates phase relations. Experimental results on mixed fluid (C–O–H) MORB compositions suggest however that, as CO₂ strongly fractionates into carbonates leaving a coexistent H₂O-rich fluid, amphibole stability is not significantly affected. Additionally, counterintuitively, the stability of lawsonite is slightly enhanced by the addition of CO₂, extending its stability to higher temperature (Poli et al., 2009). Although the stability of lawsonite is shifted by only 30–80 °C, this difference is relevant as the reaction has a slope parallel to most *P*–*T* paths, and small temperature differences control whether the rock is dry or volatiles are present in the rock.

Summarizing, hydrous phases in mafic lithologies significantly contribute to the water cycle at subduction zones: while amphibole mainly controls fluid production in the forearc region, with high dehydration rate and fluid production, lawsonite and/or zoisite governs the subarc region.

2.02.5.3 Phase Relations in Hydrous Peridotite Systems

Hydrous peridotites have been extensively investigated at near-solidus conditions (Green, 1973; Mysen and Boettcher, 1975;

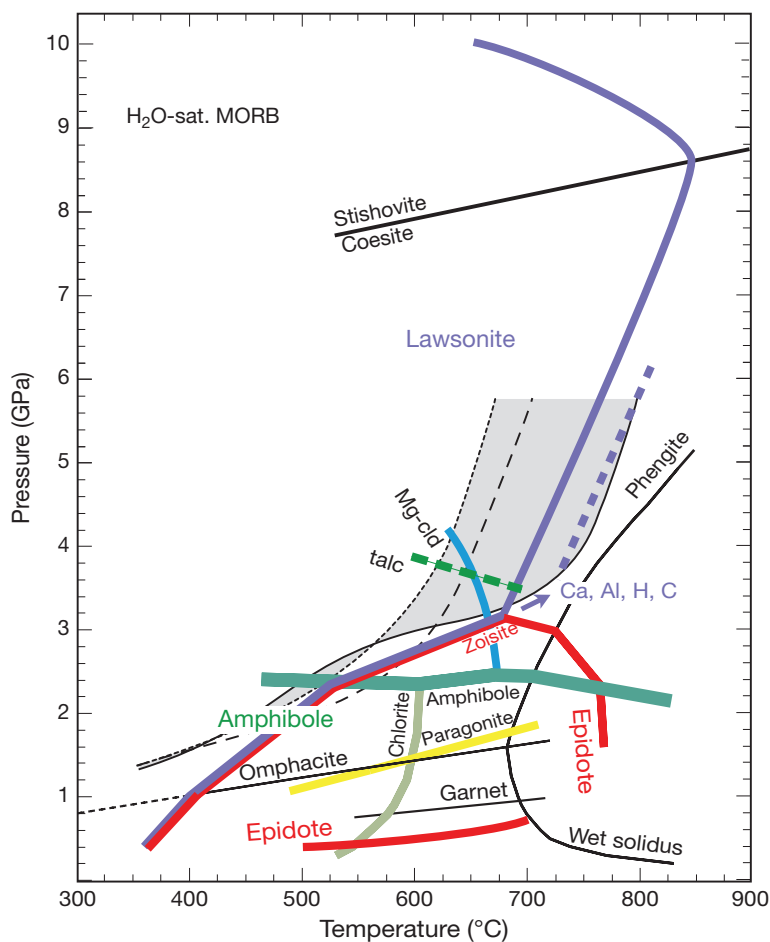


Figure 10 Experimentally derived phase diagram for H_2O -saturated mid-ocean ridge basalt (modified from Schmidt MW and Poli S (1998) Experimentally based water budgets for dehydrating slabs and consequences for arc magma generation. *Earth and Planetary Science Letters* 163: 361–379.) and at oxygen fugacity of approximately Ni-NiO buffer. Lawsonite stability is displaced toward higher temperature as anorthite (Ca, Al), H, and C increase. Shaded area represents P - T paths for slab surface from Arcay et al. (2007) with different water weakening effects: straight line represents a model reference for a 'dry' rock; dashed line refers to a moderate rock strength reduction due to water; narrow dashed line refers to a relevant strength reduction.

Niida and Green, 1999; Wallace and Green, 1991). These studies are of relevance for the melting behavior of the mantle (see this volume Chapter 2.19). The knowledge of the subsolidus phase relations is restricted to simplified chemical systems (MSH, $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ (MASH), $\text{CaO-MgO-SiO}_2\text{-H}_2\text{O}$ (CMSH), and $\text{FeO-MgO-SiO}_2\text{-H}_2\text{O}$) assumed to be representative of up to 95% of harzburgitic or lherzolititic bulk mantle or is based on a few experimental studies devoted to investigate peridotite modeled in complex, close to natural compositions (Fumagalli and Poli, 2005; Fumagalli et al., 2009; Tumiati et al., 2013).

Phase relations in hydrous peridotites are shown in Figure 11. Serpentine is the dominant hydrous mineral phase in the oceanic lithosphere at slow-spreading centers, and due to its high water content, its low density, and its low mechanical strength, it is serpentine that exerts control on subduction zones dynamics and rheology (e.g., Campione and Capitani, 2013; Hattori and Guillot, 2003; Hilalret and Reynard, 2009; Scambelluri et al., 2004). As a result, serpentine has been thoroughly investigated experimentally, focusing not only on

its stability field (Bromiley and Pawley, 2003; Ulmer and Trommsdorff, 1995; Wunder and Schreyer, 1997) but also on the kinetics of serpentine dehydration reactions (Chollet et al., 2011) and on its elastic properties, both experimentally (Hilalret et al., 2006; Nestola et al., 2010) and theoretically (Capitani and Stixrude, 2012; Capitani et al., 2009; Mookherjee and Capitani, 2011; Mookherjee and Stixrude, 2009). Nonetheless, although phase assemblages are dominated by serpentine, other hydrated minerals may persist beyond the serpentine stability field in the mantle and play a pivotal role in the dehydration and fluid production during subduction.

In the following paragraphs, we present the available experimental results on the most important hydrous phases in hydrated peridotites.

2.02.5.3.1 Talc and amphibole

Talc (4.7 wt.% H_2O , density $2.6\text{--}2.8\text{ g cm}^{-3}$) is restricted to pressures lower than 2 GPa. No significant solid solutions are expected in talc, with the exception of a moderate Tschermak substitution ($\text{Mg}^{(\text{VI})}\text{Si}^{(\text{IV})} = \text{Al}^{(\text{VI})}\text{Al}^{(\text{IV})}$). If such an exchange is

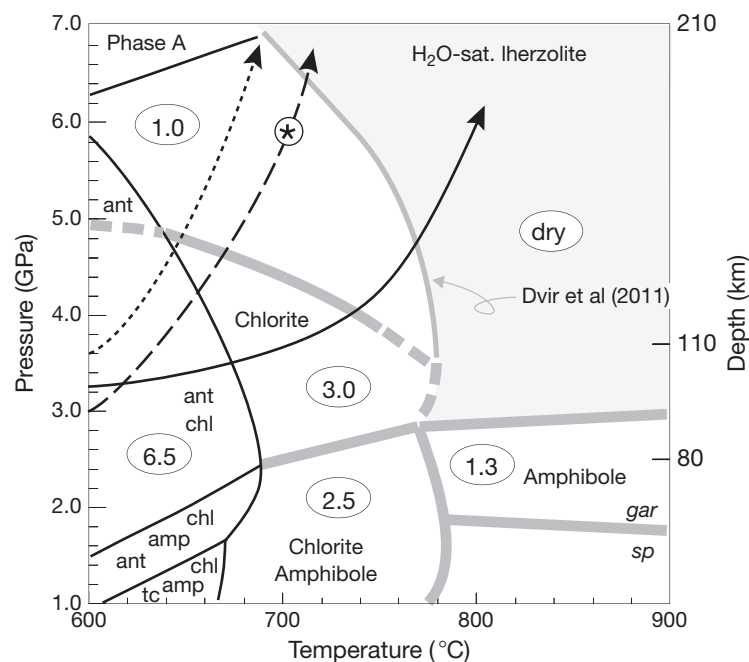


Figure 11 Experimentally derived phase diagram for H₂O-saturated Iherzolite modified from Fumagalli P and Poli S (2005) Experimentally determined phase relations in hydrous peridotites to 6.5 GPa and their consequences on the dynamics of subduction zones. *Journal of Petrology* 45: 1–24. Antigorite breakdown is from Ulmer and Trommsdorff (1995); the thermal stability of the 10 Å phase is from Dvir et al. (2011). Numbers in ovals are the estimated water content based on mass balance. *P*–*T* paths are from Arcay et al. (2007) as in Figure 10.

possible in the bulk composition, then the stability of talc is slightly extended to higher pressure. It is widely accepted that talc forms as a product of orthopyroxene alteration that leads to talc and serpentine in a mid-ocean ridge environment. However, the talc stability is strongly influenced by Si enrichment as a result of metasomatic fluids released by overlying sediments and oceanic rocks of the descending slab to mantle wedge peridotites. The talc dehydration reaction in mantle compositions is governed by the reaction talc + forsterite = clino-/orthoenstatite + fluid. This reaction has been extensively investigated in the MSH system (Bose and Ganguly, 1995; Chemosky et al., 1985; Kitahara et al., 1966; Pawley, 1998; Ulmer and Trommsdorff, 1995; Wunder and Schreyer 1997; Yamamoto and Akimoto, 1977). Despite the relatively simple chemical system in which these experiments were performed, the exact location of the dehydration reaction is not well known. Melekhova et al. (2006) explained some possible causes of different experimental results using a novel rocking piston–cylinder. Such a high-pressure apparatus enables experimentalists to avoid chemical zonation caused by the Soret effect within the experimental charge, a very common experimental problem when a fluid is involved (Schmidt and Ulmer, 2004). According to Melekhova et al., the differences in the location of the transition are related to a decrease of H₂O activity, due to a high solubility of Mg and Si in the fluid at high pressures, and to the effect of the clinoenstatite–orthoenstatite transition. This last consequence is an excellent example of the effect that anhydrous phase (orthopyroxene) may have on a dehydration reaction. Note that talc is highly anisotropic upon compression and this should have a large effect on the seismic properties of the rock (Bailey and Holloway, 2000; Mainprice et al., 2008; Stixrude, 2002).

The role of talc on seismic anisotropy is, however, expected to be a function of its modal abundance and its preferred orientation. Hacker et al. (2003) suggested that 11–15% of talc might be hosted in harzburgite and Iherzolite but up to 41% in mantle wedge assemblages related to the breakdown of serpentine.

The amphibole (~2.2 wt.% H₂O, density 2.98–3.17 g cm^{−3}) stability in the mantle is strongly dependent on bulk composition (Niida and Green, 1999), as it forms extensive solid solutions and its composition changes drastically with pressure and temperature. Up to 1.5 GPa, the entire solid solution tremolite–pargasite is stable (Jenkins, 1983). At higher pressure, amphibole is tremolite at relatively lower temperature, where it coexists with clinopyroxene and chlorite, and becomes pargasitic close to the solidus. At 700 °C, the amphibole stability boundary in Iherzolite is located at 2.5 GPa (Fumagalli and Poli, 2005). Its breakdown is related to a water-conservative reaction, that is, no release of fluids is expected during its breakdown, and consequently, water is completely transferred to chlorite at higher pressure. At higher temperature, above the stability field of chlorite, the upper pressure stability of amphibole is controlled by the reaction that leads to clinopyroxene + orthopyroxene + garnet + fluid. This reaction is strongly controlled by the Na and Ca content of the bulk composition: the highest pressure stability is in fertile compositions, with high amounts of Ca and Na, where amphibole persists at 925 °C to pressures of up to 3 GPa (Niida and Green, 1999). Investigating the role of water in Iherzolites, Green et al. (2010) determined the maximum amount of structurally bound water in amphibole before the appearance of an aqueous fluid or melt as 0.6 wt.% H₂O at 1.5 GPa, 1000 °C (i.e., hosted in 30% pargasite). The change in

amphibole mineral chemistry as a function of pressure lowers the modal abundance to 10% and as a result lowers the water storage capacity of the rock to 0.2 wt.% H₂O. Additional complexities arose by the potential dissolution of oxides, particularly of alkalis, K₂O, and Na₂O in high-pressure fluids. Green et al. (2010) found that the water/rock ratio plays a fundamental role: water contents >5 wt.% may inhibit the formation of amphibole at high *P* as alkali elements tend to partition into the vapor phase.

2.02.5.3.2 Serpentine and chlorite phase assemblages

Serpentine (13 wt.% H₂O, density 2.6 g cm⁻³), in its antigorite form, dominates the low-temperature high-pressure field and is stable up to 6 GPa (which corresponds to about 200 km depth). The stability of antigorite in complex systems, that is, natural compositions, is reasonably assumed to be that reported from experiments in the MSH systems (Bose and Ganguly, 1995; Bose and Navrotsky, 1998; Evans et al., 1976; Ulmer and Trommsdorff, 1995; Wunder and Schreyer, 1997) as no extensive solid solutions are expected for this hydrous phase. Nonetheless, Ulmer and Trommsdorff (1999) reported several discrepancies on the exact location of the upper thermal stability of antigorite. One of the main causes for these discrepancies could be down to the effect of minor components such as Cr, Fe, and Al, on the stability of serpentine. Bromiley and Pawley (2003) confirmed this, reporting a slightly increased thermal stability of antigorite due to addition of Al. The choice of the stability field adopted to envisage physical properties within the mantle should therefore be made by keeping in mind that different bulk compositions (pure antigorite vs. Cr-, Fe-, Al-bearing antigorite solid solution) have been used. At higher pressure, antigorite is replaced by a dense hydrous magnesium silicate (DHMS), the so-called phase A (Bose and Ganguly, 1995) and, even deeper in the transition zone, by phase E.

In deeper parts of the mantle, when Al is considered, chlorite (13 wt.% H₂O, 2.6–3.3 g cm⁻³) can store water up to temperatures and pressures beyond the stability of antigorite and amphibole. Chlorite has been extensively investigated in the simplified MASH system (Chernosky, 1974; Fawcett and Yoder, 1966; Fockenberg, 1995; Jenkins and Chernosky, 1986; Staudigel and Schreyer, 1977; Ulmer and Trommsdorff, 1999). However, in contrast to talc and antigorite, chlorite is expected to form extensive solid solutions, for example, hosting Fe or Cr in its structure. As a result, phase relations are expected to be strongly affected by increasing chemical complexity of the system.

The thermal stability of chlorite in mantle rocks is related to the breakdown of chlorite + pyroxene, via reactions (e.g., chlorite + pyroxene = olivine + garnet + water) that systematically occur at slightly lower temperature as compared with the thermal terminal stability of pure chlorite (chlorite = forsterite + pyrope + spinel + water). Fumagalli and Poli (2005) found that chlorite stability in lherzolite is shifted toward slightly lower temperature as a result of preferential partitioning of Fe into garnet and mass balance calculations on high-pressure experiments suggested the relevant role of clinopyroxene and grossular component in garnet in the thermal stability of chlorite. Despite the fact that Cr is a minor constituent in the Earth's mantle, due to its uneven partitioning among major mantle minerals, MASH phase equilibria are expected to be strongly

displaced (Chatterjee and Terhart, 1985) due to the presence of Cr. High-pressure mantle chlorites, found in natural peridotites, host up to 2.0 wt.% Cr₂O₃ (Ravna, 2006); intermediate content of Cr₂O₃ (up to 5–6 wt.%) has been reported for chromian chlorite found in veins in association with chromite deposits and ultramafic rocks (e.g., Nuggihalli Schist Belt, India – 5.18 wt.% Cr₂O₃, Phillips, 1980). In experiments, Grove et al. (2006) and Till et al. (2012) synthesized mantle chlorites in primitive mantle composition (Hart and Zindler, 1986) containing up to 1.47 wt.% Cr₂O₃ at 3.6 GPa, 800 °C, suggesting that Cr₂O₃ solubility in chlorite is expected to enlarge its thermal stability. More recently, Fumagalli et al. (2014) found that in the simple Cr-MASH system, chlorite in mantle assemblages can host up to 2.2 wt.% Cr₂O₃ and that its stability is enhanced by 50 °C per 0.5 GPa.

2.02.5.3.3 Post antigorite–chlorite hydrous phases

At higher pressure, phase equilibria are complicated by the somewhat uncertain fate of chlorite and antigorite stability. Several hydrated minerals have been synthesized as products of breakdown reaction of antigorite and chlorite: phase A, the 10 Å phase, Mg-sursassite (formerly called MgMgAl-pumpellyite), and a newly found pyroxene-like hydrous structure, called phase-HAPY (hydrous Al-bearing pyroxene) (Gemmi et al., 2011). While chlorite-bearing peridotite and serpentinite have often been found in nature, all other hydrates have only been synthesized in high-pressure laboratories. However, the 10 Å phase has recently been found as inclusions in olivine crystals from ultrahigh-pressure rocks (Khishina and Wirth, 2008). Although it is obvious that DHMS play an important role at lower mantle conditions, the stability of the 10 Å phase and of phase A as reaction product of chlorite and antigorite breakdown, respectively, underlines that these hydrous phases are also relevant in the upper mantle.

The stability of phase A (11.8 wt.% H₂O, density 2.96 g cm⁻³) has been determined in the simple systems MSH and MASH (Luth, 1995; Ulmer and Trommsdorff, 1995). It was found that at 800 °C phase A is stable between 7 and 10 GPa. In peridotite bulk compositions, however, the stability of phase A together with enstatite at 1050 °C is extended to 6–13 GPa (Kawamoto, 2004; Kawamoto et al., 1995). At lower temperature, antigorite assemblages transfer directly H₂O to phase A-bearing assemblages (Bose and Ganguly, 1995).

If higher temperatures are considered, additional and intermediate hydrous phases have been found. The 10 Å phase (8–13 wt.% H₂O, density 2.7) was first synthesized in the MSH system (Sclar et al., 1965) and has been extensively investigated in the last decades both experimentally (Chinnery et al., 1999; Chollet et al., 2009; Comodi et al., 2005, 2006; Fumagalli et al., 2001; Pawley and Wood, 1995; Pawley et al., 2011; Welch et al., 2006) and theoretically (Bridgeman and Skipper, 1997; Bridgeman et al., 1996; Fumagalli and Stixrude, 2007; Wang et al., 2004). The 10 Å phase is a phyllosilicate 2:1 with interlayer stably bound water molecules. Fumagalli et al. (2001) performed time-resolved experiments and found that this phase might host a variable amount of water and exhibits a swelling behavior that enables it to incorporate large molecules within its interlayer. The relevance of the 10 Å phase in ultramafic

rock compositions is strongly related to the talc appearance, as this phase is compositionally a hydrated form of talc. As a result, its presence is expected in Si-enriched bulk compositions, formed as a result of complex fluid/rock interactions at subduction zones. However, the reconnaissance of an Al-bearing 10 Å phase in peridotite systems stable at the expense of chlorite at 4.8 GPa, 650 °C, emphasizes the relevance in the ultramafic portion of the slab for the water budget of subducting slabs. Dvir et al. (2011) investigated the compositions of coexisting fluids in peridotitic compositions up to 6 GPa. They confirmed the stability of this phase in mantle phase assemblages and further constrained its thermal stability, governed by the reaction $10\text{ Å phase} + \text{clinopyroxene} = \text{garnet} + \text{orthopyroxene} + \text{H}_2\text{O}$, between 750 and 800 °C, at 5 GPa. Note that the replacement of chlorite-bearing assemblages with 10 Å phase-bearing rocks is not well understood, yet. Fumagalli and Poli (2005) suggested either a solid solution relation, implying a continuous reaction from chlorite to the Al-bearing 10 Å phase structure, or a more complex structural rearrangement as mixed layered structure with chlorite and 10 Å phase interconnected at the nanoscale following order–disorder relations. Additionally, its stability field overlaps those of other hydrates such as phlogopite, and high-pressure experimental results, based on the peculiar mineral chemistry of high-pressure low-temperature phlogopite (see later), would suggest possible structural relations between 10 Å phase and phlogopite. The 10 Å phase thus plays an important role in transferring water into the deeper mantle of the Earth not only persisting as single phase beyond the stability of serpentine and chlorite but also, possibly, entering the structure of other hydrates such as chlorite and phlogopite.

Mg-sursassite (7 wt.% H_2O , density 3.3 g cm^{-3}), previously known as MgMgAl-pumpellyite, was first synthesized by Schreyer et al. (1986) at 5.0 GPa, 700 °C, and subsequently characterized by Bromiley and Pawley (2002), Gottschalk et al. (2000), and Grevel et al. (2001). Experimental studies demonstrated that Mg-sursassite is stable over a wide range of temperature, from 3.5 to 10 GPa (Fockenberg, 1995) and therefore it could play a relevant role in subduction zone environment. Its stability (in end-member composition) represents, however, a maximum stability field; in ultramafic composition, Mg-sursassite is precluded by the simultaneous stability of pyrope plus water assemblages (Artioli et al., 1999; Fockenberg, 1998; Ulmer and Trommsdorff, 1999) and its stability is likely to be reduced. Nevertheless, Mg-sursassite is considered of relevance in transferring water from antigorite–chlorite bearing assemblages to other hydrates stable at higher pressure such as phase A via reaction $\text{Mg-sursassite} + \text{forsterite} = \text{phase A} + \text{enstatite} + \text{pyrope}$ by which no fluid is released and H_2O content is completely transferred to phase A-bearing assemblages. Mg-sursassite in ultramafic is expected to form from chlorite-bearing assemblages via reaction $\text{chlorite} + \text{enstatite} = \text{Mg-sursassite} + \text{forsterite} + \text{fluid}$. This reaction implies that out of the 2.8 wt. % of H_2O contained in a chlorite peridotite, only the 0.98% is retained in Mg-sursassite (Luth, 2003). The effect of additional components has been experimentally investigated by Wunder and Gottschalk (2002) who reported the synthesis of Fe–Mg-sursassite. Fe-bearing systems are of relevance as results would

shed light on the influence of Mg–Fe partitioning on the stability of high-pressure Mg-sursassite.

A previously unknown hydrous phase, a HAPY (the so-called ‘HAPY’ phase, 7 wt.% H_2O , density 3.14 g cm^{-3}), was recently found in the MASH, MSH, and Cr–MASH systems as product of chlorite breakdown at 5.4 GPa, 720 °C (Fumagalli et al., 2014). Its crystal structure, characterized by automated electron diffraction tomography (Gemmi et al., 2011), is a single-chain inosilicate resembling the pyroxene structure but containing three independent cation sites. The stability of phase HAPY is far from being understood, but it might interact with other hydrates stable in the MASH system (e.g., phase A, Mg-sursassite, and 10 Å phase) at comparable and overlapping pressure and temperature conditions. Furthermore, from structural considerations, phase-HAPY might be able to host several additional cations via substitution such as Fe, Ca, Mg, or Tschermak exchange, making this phase of relevance in more complex systems. The discovery of phase HAPY in the MASH/Cr–MASH systems has two important implications: (i) It is a hydrous phase that persists beyond the stability of chlorite and/or antigorite and it is able to host much more water than NAMs. (ii) It has a particularly high density, higher than DHMS such as phase A and 10 Å phase, and as a result, it might contribute considerably to slab pull processes in subduction zones. However, its composition ($\text{MgO}:\text{Al}_2\text{O}_3:\text{SiO}_2 = 2:2:1$) falls in the $\text{MgO}:\text{SiO}_2 > 1$ portion of the MASH system. As a result, its stability is restricted to unusual bulk compositions in the mantle, and it is precluded when the pyrope + enstatite + fluid assemblage is stable.

In addition, the role of minor components in stabilizing additional hydrates able to storage water at post serpentine assemblages should be taken into account. The natural occurrence of Ti-clinohumite in ultrahigh-pressure metamorphic rocks initiated high-pressure experiments on the stability of humite-structured minerals. Stalder and Ulmer (2001), examining the stability of post antigorite phases up to 15 GPa, showed that the thermal stability of humite minerals is greatly enhanced by small amount of minor component such as F. Furthermore, the F/OH ratio in clinohumite decreases with pressure. Note that the F content of naturally occurring clinohumite from Cima di Gagnone, Switzerland (Evans and Trommsdorff, 1983), seems to indicate a pressure of origin as high as 5 GPa.

Both phase A and clinohumite are unstable above 14 GPa, and in peridotite compositions, they are replaced by the assemblage phase E + forsterite + enstatite that persists up to the transition zone at 400 km of depth.

2.02.5.4 Fluid/Rock Interactions and the Role of Potassic Hydrous Phases

In subduction zones, the extreme variability of bulk compositions and the complex relations among fluids and mantle minerals indicate that hybrid mantle compositions are common, which include chemical elements that are not commonly enriched in normal mantle compositions. Metasomatic processes are known to cause this element enrichment. Such processes in the mantle have been recognized for a long time and were documented mainly by studies on mantle xenoliths (e.g.,

Nixon, 1987). However, the geochemistry of the slab–mantle interface is known to be controlled by the interaction of high-pressure fluids, crustal components, and ultramafic lithologies. Peridotite bodies may intrude into subducting continental crust as a result of buoyancy forces acting at the interface (Brückner, 1998). As a result, the devolatilization of felsic rocks and mass transfer toward peridotite are strongly enhanced, and a variety of volatile-bearing phases are stabilized in mantle rocks. Ti-phlogopite and diamond inclusions in Bardane peridotite, Norway (e.g., van Roermund et al., 2002), document the importance of metasomatic mass transfer and hybridization of upper mantle lithologies at depth. Phlogopite–spinel peridotites (Nixon, 1987), phlogopite–garnet peridotites, phlogopite–K-richertite peridotite xenoliths, and ‘orogenic’ phlogopite peridotites of ultrahigh-pressure terrains (Ultrat peridotite: Rampone and Morten, 2001; Bardane peridotite, Norway: van Roermund et al., 2002; Sulu garnet peridotite, China: Zhang et al., 2007) document that such a process might occur both within the mantle wedge and at the slab–mantle interface, also at relatively low temperatures.

The stability of potassic phases in mantle rocks has been experimentally investigated both in relatively simple systems considering phlogopite alone, phlogopite + forsterite, and phlogopite + enstatite + diopside (Luth, 1997; Sudo and Tatsumi, 1990) and in bulk rocks similar to K-enriched lherzolites (Conceição and Green, 2004; Fumagalli et al., 2009; Konzett and Fei, 2000; Konzett and Ulmer, 1999; Mengel and Green, 1989; Wendlandt and Eggler, 1980). Phase relations are governed by the occurrence of three potassic phases, which are in order of pressure stability: phlogopite, a potassic amphibole of richteritic composition (K-amphibole), and a K-rich hydrous silicate, termed phase X ($K_{2-x}Mg_2Si_2O_7H_x$, $x=0-1$; Yang et al., 2001). In K-enriched lherzolite, phlogopite coexists with Ca-amphibole up to 3.2 GPa and 900 °C (Fumagalli et al., 2009). However, although the pressure stability of Ca-amphibole is slightly enhanced by the addition of K, its breakdown at relatively low-temperature conditions is controlled by a water-conservative reaction that leads to newly formed phlogopite but does not necessarily imply release of a free fluid phase. K-amphibole represents the breakdown product of phlogopite-bearing assemblages and phase X represents the breakdown product of K-amphibole. The potassic amphibole, which forms at the expense of phlogopite, is an Al-poor potassic amphibole and appears between 6 and 6.5 GPa at 800 °C and between 6.5 and 7.0 GPa at 1100 °C (Konzett and Ulmer, 1999). At pressures above 13–14 GPa (1100 °C), phase X is known to replace K-amphibole. In more complex chemical compositions, the breakdown of K-amphibole occurs at lower pressures. The K-amphibole to phase X transition involves a continuous change of garnet compositions through Ca–Mg exchange and some limited majorite component (Konzett and Fei, 2000).

The thermal stability of K-amphibole is determined by the appearance of the anhydrous assemblage garnet, olivine, orthopyroxene, and clinopyroxene. In the K_2O – Na_2O –CMASH system, it occurs between 1300 and 1400 °C at 8.0 GPa and shows a positive Clapeyron slope. However, in an Fe-bearing system and in lherzolitic compositions, the effect of iron has to be taken into account. Konzett and Ulmer (1999) investigated a K-doped lherzolite modifying the composition of the Mont

Briançon lherzolite (Massif Central, France) by adding phlogopite or K-richertite (see Table 1) components. In the lherzolitic system, the K-amphibole in reaction slightly shifts toward lower pressure (between 6.0 and 6.5 GPa at 1100 °C) due to the preferential partitioning of Fe^{2+} into garnet, which is a product of phlogopite breakdown. The coexistence of phlogopite and K-amphibole is, however, reduced to less than 1 GPa. Konzett and Fei (2000) conducted experiments using a K-amphibole-enriched peridotite (KLB-1) from 12 to 14 GPa and 1200 °C. Potassic phases, either K-amphibole or phase X, were found to coexist with garnet, low-Ca clinopyroxene, high-Ca clinopyroxene, and forsterite. In the Fe-bearing system, the K-amphibole to phase X transition, occurring between 12 and 13 GPa at 1200 °C, is shifted by about 1.0 GPa toward lower pressure as compared with what was found in the Fe-free system.

K-enriched lherzolite compositions were also investigated at relatively lower temperature (Fumagalli et al., 2009) and in the presence of C–O–H fluids (Tumiati et al., 2013). As a result of the increase of the content of alkali elements, the amphibole stability is enhanced at higher pressure, with a maximum of 3.4 GPa at 880 °C. In K-enriched lherzolite with C–O–H fluids, carbonates such as magnesite and dolomite appear, but the location of the amphibole out reaction remains unchanged. At relatively low temperatures, relevant to the conditions of the slab–mantle interface, the phlogopite mineral chemistry is unusual. An excess in Si and a deficit in Al and Na + K suggest a significant talc component in phlogopite, probably as a result of mixed layers in the phlogopite structure and the hydrated form of talc, that is, the 10 Å phase (Fumagalli et al., 2009). The chemical variability of phlogopite implies a continuous reaction responsible for the breakdown of amphibole that does not release a free fluid phase. Furthermore, the modal abundance of phyllosilicates is strongly enhanced at lower temperatures, that is, at the slab–mantle interface, reaching 7 wt.% modal as compared with 2 wt.% at relatively shallow depth within the stability of Ca-amphibole. Fumagalli et al. (2009) suggested that the K/OH ratio may be used to indicate the ability of a release of fluid via the transition from phlogopite to K-amphibole: At mantle wedge conditions, the K/OH ratio of phlogopite and the higher-pressure potassic phase is similar and therefore a water-conservative reaction is expected with no release of fluids. As the K/OH ratio of phlogopite is decreasing, at fixed K content in K-amphibole, a large release of fluid is expected (Figure 12).

2.02.5.5 Implications to the Geodynamics of Subduction Zones

Here, we compare experimentally derived phase diagrams with P – T paths for slab surfaces in subduction zones (Figure 11). The thermomechanical model of Arcay et al. (2007) focuses on the degree of mechanical coupling between the slab and the mantle wedge and results in high thermal gradients within the lithosphere. Different paths take into account different amounts of water that weaken mantle rocks. Although these are typically cold thermomechanical models, they exhibit the different roles that hydrous phases can play in subduction processes rather well. Although antigorite dominates the water budget up to at least 2 GPa (Figure 11), in fertile

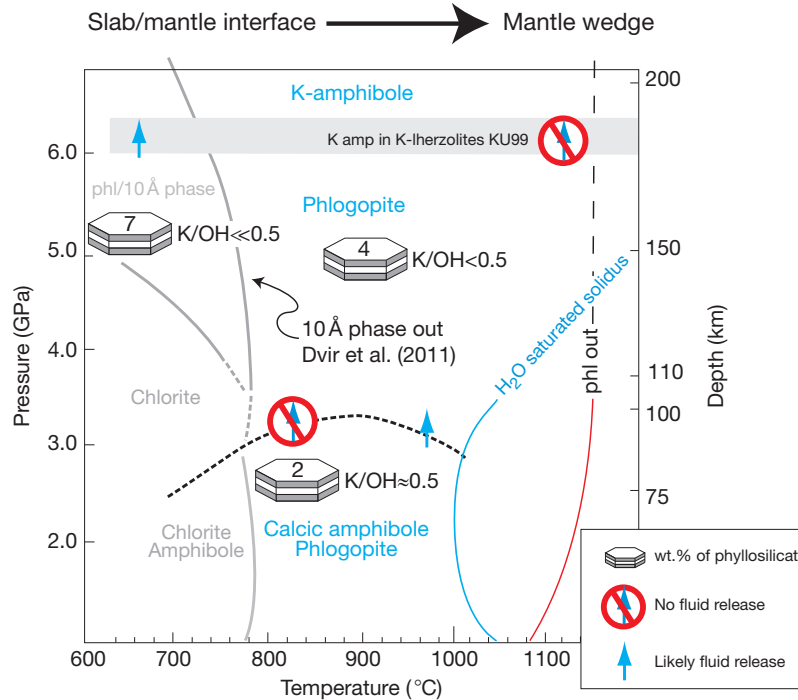


Figure 12 Experimentally derived phase relations for a K-doped H₂O-saturated Iherzolite modified from Fumagalli P, Zanchetta S, and Poli S (2009) Alkali in phlogopite and amphibole and their effects on phase relations in metasomatized peridotites: A high-pressure study. *Contributions to Mineralogy and Petrology* 158: 723–737. Phlogopite modal abundance is maximum at slab/interface conditions. The K/OH ratio of phases controls the fluid production. At low temperature, the transition Ca-amphibole/phlogopite does not necessarily imply fluid release; on the other hand, as a result of the reduced K/OH in the phyllosilicate, the transition phlogopite/K-amphibole at low temperature is likely associated to a fluid flux.

Al-bearing Iherzolite, the occurrence of first chlorite and later the 10 Å phase at higher pressures opens a new scenario to the transfer of volatiles deep into the mantle. The 10 Å phase acts as a bridge, transferring water from antigorite–chlorite-bearing assemblages to phase assemblages typical of the transition zone and the lower mantle. However, this occurs when the thermal regime is such that the antigorite breakdown occurs at pressure higher than 6 GPa (Bose and Ganguly, 1995; Bose and Navrotsky, 1998). In such a case, no relevant fluid flux is expected, and water is transferred first to the 10 Å phase and then to phase A-bearing assemblages, down toward the lower mantle. In contrast, if the *P*–*T* path intersects the stability field of antigorite at pressure <6 GPa (path * in Figure 11), volatiles are first transferred to chlorite and the 10 Å phase and then released over a depth interval of about 20–30 km, with fluid production directly related to the stability of chlorite and the 10 Å phase at higher pressure.

Serpentine has been widely regarded as the main hydrate responsible to trigger intermediate depth earthquakes at DSZs (Dorbath et al., 2008; Kirby et al., 1996; Peacock, 2001; Yamasaki and Seno, 2003). Experimentally derived phase diagrams however suggest that if this is the case, then a cold thermal regime is required and a high degree of hydration and/or an Al-poor bulk composition is needed (Fumagalli and Poli, 2005). On the other hand, if Al-rich compositions are considered, then at low degree of hydration prior to subduction, chlorite or the 10 Å phase is stable rather than antigorite. In this case, a complete dehydration of the slab is expected, and the effect of dehydration embrittlement used to reconcile deep seismicity with the petrology of the slab should be attributed to the chlorite/10 Å phase breakdown (Figure 13).

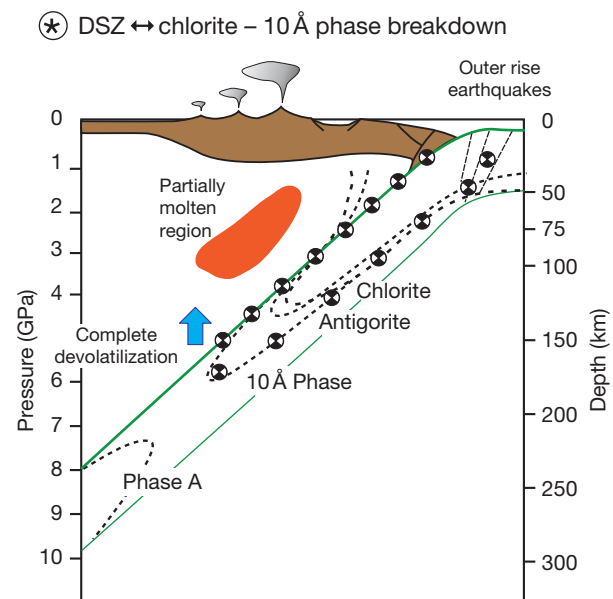


Figure 13 Relations between the thermal structure of a subduction zone, the stability field of hydrates in the ultramafic portion of the slab, and the location of arc volcanism. Modified from Fumagalli P and Poli S (2005). Experimentally determined phase relations in hydrous peridotites to 6.5 GPa and their consequences on the dynamics of subduction zones. *Journal of Petrology* 45: 1–24. Earthquake focal mechanisms are not indicating the kinematics, but only the location of double seismic zones (DSZs). If H₂O undersaturation and relatively Al-rich compositions prevail, the DSZ can be only related to the dehydration of the chlorite/10 Å phase breakdown and a relatively hotter thermal structure is expected (path (*) in Figure 11).

2.02.6 Conclusions

We present mainly experimental results on how the mineralogical composition of upper mantle rocks is related to changes of pressure, temperature, and chemical composition. We show that experiments in chemically simplified compositions define phase transitions and phase reactions. These experiments in simple systems need to be followed by further experiments that define the effect of minor components such as Cr, Fe, alkalis, or volatile elements on mineral stability, melting relationships, and phase transformations. Here, we show that minor chemical components can have a major influence on phase assemblages or physical properties of rock. As a consequence, when the physical properties of mantle rocks are calculated or modeled, care should be taken to choose a bulk composition that is relevant to the rocks one wishes to investigate.

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2.03 Phase Transitions and Mineralogy of the Lower Mantle

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2.03.1 Introduction

Until recently, experimental high-pressure mineral physics studies mainly focused on materials in the upper part of the mantle because of technical restrictions in pressure and temperature generation and also in precise measurements of crystal structures and physical properties under the lower mantle conditions. However, developments in technologies of both laser-heated diamond anvil cell (LHDAC) and large-volume Kawai-type multianvil apparatus (KMA), combined with synchrotron radiation, have enabled us to quantitatively study phase transitions and some key physical properties of mantle minerals under the P , T conditions encompassing those of the whole mantle.

Progress in computational mineral physics based on ab initio calculations has also been dramatic in the last two decades in conjunction with the rapid advancement of computer technologies. Classical molecular dynamics calculations required a

priori assumptions about the parameters for interatomic model potentials, which largely rely on available experimental data. Quantum mechanical Hamiltonians of many-body electron systems can be efficiently and quantitatively evaluated on the basis of the density functional theory (DFT) (Hohenberg and Kohn, 1964; Kohn and Sham, 1965). Practical calculations of minerals that have complex crystal structures can be achieved using various methods and techniques developed following the DFT. As a result of such advancement in ab initio calculations, it is now possible to predict stability and some physical properties of high-pressure forms quantitatively with uncertainties that are comparable to those in experimentally derived data, as was dramatically shown in a series of recent articles related to the postperovskite (PPv) phase transition (Iitaka et al., 2004; Oganov and Ono, 2004; Tsuchiya et al., 2004a,b).

Another reason for the relatively scarce mineral physics studies for the lower part of the mantle may originate from the fact that there has been no indication of the occurrence of

major phase transitions under these conditions, except for those corresponding to the uppermost (~ 660 – 800 km) and lowermost (~ 2700 – 2900 km; the D'' layer) parts of the lower mantle. This is in marked contrast to the nature of the mantle transition region, best described as 'the key to a number of geophysical problems' by Birch (1952). Recent seismological studies, however, demonstrated that there are regions that significantly scatter seismic waves, which may be related to some unknown phase transitions and/or chemical boundaries at certain depths in the upper to middle regions of the lower mantle (e.g., Niu and Kawakatsu, 1996). In addition, both geochemical considerations and mantle dynamics simulations suggest that the mantle may be divided into chemically distinct regions by a boundary at a depth of 1500 – 2000 km in the lower mantle (e.g., Kellogg et al., 1999; Tackley, 2000; Trampert et al., 2004). Moreover, seismological studies with various methods of analysis have shown detailed structures in the D'' layer, demonstrating marked heterogeneity in both horizontal and vertical directions (Lay et al., 2004). Thus, there is growing evidence that the lower mantle is not featureless any more, and many mineral physicists have started to develop experimental and computational techniques for higher pressure and temperature conditions (with improved accuracy) in order to elucidate the mineralogy of the lower mantle.

In spite of the great efforts in both experimental and theoretical studies (mostly conducted in the last two decades), our knowledge of the stability and mineral physics properties of high-pressure phases relevant to the lower mantle is still very limited compared with that of the shallower parts of the mantle. Although LHDACs are now capable of generating pressures and temperatures corresponding to those of the central region of the Earth's interior (Tateno et al., 2010), there remain a number of disagreements in phase equilibrium studies using this method with various techniques in heating, temperature/pressure measurements, phase identification, and so on. Mineral physics parameters that constrain densities of high-pressure phases in the lower mantle have been defined thanks to intense synchrotron sources, particularly those available at third-generation synchrotron facilities, such as ESRF, APS, and Spring-8, combined with both LHDAC and KMA, but those related to elastic wave velocities are scarce to date.

In this chapter, we briefly review recent progress and limitations in experimental and computational techniques in studying phase transitions and some key physical properties under the lower mantle conditions. Then, we summarize current knowledge of these properties obtained experimentally and/or theoretically using these techniques. We focus on the phase transitions and phase relations in simple silicates, oxides, carbonates, and hydrous systems closely related to the mantle and slab materials, because experimental measurements or theoretical predictions of other properties such as shear moduli and their pressure/temperature dependency are still limited, particularly for the conditions of the deeper regions of the lower mantle. In contrast, equation of state (EoS) parameters, that is, zero-pressure densities, bulk moduli, and the pressure/temperature dependencies of some of the high-pressure phases, are summarized as far as reliable data are available. We also review the phase transitions and density changes in lithologies associated with the subduction of slabs

and also those in the surrounding model mantle materials on the basis of experimental results on multicomponent systems. Some implications for the mineralogy of the lower mantle are discussed based on these data and those obtained for the simpler systems.

2.03.2 Experimental and Theoretical Backgrounds

2.03.2.1 High-Pressure Technology

Two kinds of high-pressure devices, LHDAC and KMA, have been used to realize static high-pressure and high-temperature conditions of the lower mantle in the laboratory. The upper limit of high-pressure generation in LHDAC has been dramatically expanded using a smaller anvil top (culet) with various shapes for utilizing the potential hardness of a single-crystal diamond. As a result, pressures of multi-megabars can now be comfortably generated in many laboratories. Moreover, quasihydrostatic pressures can be generated by introducing gas pressure media, such as Ar or He, which also serve as thermal insulators when heating samples with laser beams (Chapter 2.12).

The quality of heating of samples in LHDAC has also been substantially improved using various laser sources, such as YAG, CO₂, and YLF, with higher powers and more sophisticated computer-controlled feedback systems, as compared with laser heating in the early stages of its development during the 1970s and 1980s. These can now yield a stable high temperature in a sample as small as several tens of micrometers in diameter and even less thickness.

Pressures produced in KMA studies (Kawai and Endo, 1970) using conventional tungsten carbide anvils have long been limited to 25 – 30 GPa, although the relatively large sample volume in this apparatus made it possible to precisely determine the phase transitions, some physical properties, melting temperatures, element partitioning, etc., of high-pressure phases. Temperatures up to 3000 K are also produced stably for hours or even a few days using various forms of heaters, such as C, LaCrO₃, TiC, WC, and some refractory metals. In addition, both temperature and pressure gradients within the sample in KMA are believed to be far smaller than those in LHDAC.

Introduction of harder materials, that is, sintered bodies of polycrystalline diamonds (SD) with some binders, such as Co and Si, as the second stage anvils of KMA has dramatically changed this situation. Using relatively large SD anvil cubes of over 10 mm in edge length, pressures approaching 100 GPa are now produced in some laboratories using KMA (e.g., Ito, 2012; Ito et al., 2005; Tange et al., 2008), without sacrificing the advantage of the relatively large sample volumes in this apparatus. However, the limitations in hardness of SD, as compared to those of pure diamond, should restrict their use as anvils up to around this pressure. On the other hand, nanopolycrystalline diamond (NPD) converted directly from graphite at high pressure and temperature was found to be far harder than SD, and even harder than single crystal diamond (Irifune et al., 2003). The NPD rod samples as large as 1 cm in both diameter and length are now produced on a routine basis (Irifune et al., 2013), which may provide novel anvil material for higher pressure generation in KMA.

Applications of synchrotron radiation to both LHDAC and KMA started in the mid-1980s, when the second-generation

synchrotron sources became available worldwide (e.g., Shimomura et al., 1984). A combination of white x-ray and an energy-dispersive system has been used for KMA experiments at synchrotron facilities, because geometrical constraints imposed by the tungsten carbide anvils and surrounding guide-block systems make it difficult to conduct angle-dispersive diffraction measurements. Use of the energy-dispersive method combined with a multichannel analyzer has the merit of rapid acquisition and analysis of x-ray diffraction data, so that real-time observations of phase transitions are possible under high pressure and high temperature. Although this method is not very suitable for the precise determination of crystal structures (due to relatively low spatial resolutions in the diffraction peak position and also to significant variations in background x-ray with the energy range), some attempts have been successfully made to make crystal structure refinements using combined step scanning and energy-dispersive measurements (Wang et al., 2004). Moreover, developments of an imaging plate (IP) detector and, more recently, x-ray CCD camera (e.g., Hamaya et al., 1996) combined with high-energy monochromatic x-ray allows us to quickly acquire x-ray diffraction from the sample in KMA with an angle-dispersive method, leading to precise diffraction measurements with relatively short acquisition time.

Identification of the phases present and precise determinations of the lattice parameters, and hence unit-cell volumes, of the high-pressure phases can be made by in situ x-ray diffraction measurements. The in situ pressure can also be monitored by the unit-cell volume changes in some reference materials, such as NaCl, Au, Pt, and MgO, using an appropriate EoS. Thus, the phase boundaries and the P , V , T relations of a number of high-pressure phases relevant to lower mantle mineralogy have been determined by in situ x-ray measurements using KMA, although there remain some uncertainties in the estimated pressures due to the lack of reliable pressure scales, as reviewed later, particularly at the pressures of the deeper parts of the lower mantle. The effect of pressure on the electromotive force of a thermocouple is another unresolved issue, which may yield an additional uncertainty in the pressure estimation based on these EoSs.

Corresponding in situ x-ray observations have also been made using LHDAC. As the geometrical restrictions on the x-ray paths are not as severe in this device, x-ray diffraction is measured with an angle-dispersion method using monochromatized x-ray. The x-ray beam is focused to generally ~ 10 – $20\ \mu\text{m}$ with collimating mirrors, and directed to the disk-shape sample with diameters of ~ 20 – $200\ \mu\text{m}$, depending on pressure ranges. YAG or ILF lasers with beam sizes of ~ 10 to several tens μm are used in most of the synchrotron facilities. By adopting IP or x-ray CCD cameras for x-ray exposure combined with data processing systems, rapid data acquisition and reductions are also possible. Thus, the phase identification and measurements of unit-cell parameters of high-pressure phases can be made by the combination of LHDAC and synchrotron radiation at pressure and temperature conditions corresponding to the entire mantle (e.g., Murakami et al., 2004a) and even to the inner core (e.g., Tatenio et al., 2010).

The major uncertainty in the in situ x-ray observations with LHDAC arises from the possible large temperature gradients in the small thin sample. Some studies demonstrated that variations of temperature are not very large in the radial direction of

the disk-shape sample, suggesting that the temperature uncertainty may be on the order of $\sim 10\%$ or less of the nominal values if the diameter of the laser beam is significantly larger than that of the x-ray beam (Shen et al., 2001). However, the temperature gradient in the axial direction of the sample can be substantially larger than this estimation (Irifune et al., 2005), depending on the nature and thickness of the thermal insulator or pressure medium, as diamond has very high thermal conductivity. Efforts have been made to overcome this issue by either coating the sample with some metal of high thermal conductivity (Sinmyo et al., 2008) or using ‘nano-beams’ far less than $100\ \text{nm}$ (e.g., Ice et al., 2010) to reduce the effects of thermal gradients in the sample.

2.03.2.2 Ab Initio Calculation

Ab initio approaches are those that solve the fundamental equations of quantum mechanics with a bare minimum of approximations. DFT is, in principle, an exact theory for the ground state and allows us to reduce the interacting many-electron problem to a single-electron problem (the nuclei being treated as an adiabatic background). A key to the application of DFT in handling the interacting electron gas was given by Kohn and Sham (1965) by splitting the kinetic energy of a system of interacting electrons into the kinetic energy of noninteracting electrons plus some remainder, which can be conveniently incorporated into the exchange-correlation energy.

The local density approximation (LDA) (Kohn and Sham, 1965) replaces the exchange-correlation potential at each point with that of a homogeneous electron gas with a density equal to the local density at the point. The LDA works remarkably well for a wide variety of materials, especially in the calculations of equations of state, elastic constants, and other properties of silicates. Cell parameters and bulk moduli obtained from well-converged calculations often agree with the experimental data within a few percent and $\sim 10\%$, respectively. Agreement with the laboratory data is not perfect, however, and some systematic discrepancies are noted for some materials.

Attempts to improve LDA via introducing nonlocal corrections have yielded some success. The generalized gradient approximation (GGA) (Perdew et al., 1992, 1996) is a significantly improved method over LDA for certain transition metals (Bagno et al., 1989) and hydrogen bonded systems (Hamann, 1997; Tsuchiya et al., 2002, 2005a). There is some evidence, however, that GGA improves the energetics of silicates and oxides but the structures can be underbound. The volume and bulk moduli calculated with GGA tend to be larger and smaller, respectively, than those measured experimentally (Demuth et al., 1999; Hamann, 1996; Tsuchiya and Kawamura, 2001). Considering the thermal effect with zero-point motion, LDA provides the structural and elastic quantities much closer (typically within a few percent) to experimental values than those obtained with GGA. In addition, a discrepancy of about 10 – $15\ \text{GPa}$ is usually seen in transition pressures calculated with LDA and GGA (Hamann, 1996; Tsuchiya et al., 2004a,c), which provide lower and upper bounds, respectively. Experimental transition pressures are usually found between the values obtained with LDA and GGA, although GGA tends to provide the pressure with better fit to the experimental value than LDA (Hamann, 1996; Tsuchiya et al., 2004a,c). The main

source of computational error can be attributed to how to treat the exchange-correlation potential.

The standard DFT has limitations in applying to Fe-bearing oxides and silicates in the following case. One-electron approximation with the standard DFT approaches fails to describe the electronic structure of Fe–O bonding correctly due to its strongly correlated behavior. Both LDA and GGA usually produce metallic bands for Fe–O bonding in silicates. They also do not provide the correct crystal field effects that break the d orbital degeneracy. More sophisticated classes of technique, such as LDA+U, LDA+DMFT (dynamical mean-field theory), multireference configurational interaction, etc. are needed to treat the many-body effect of electrons more accurately and to investigate geophysically important iron-bearing systems.

Among these schemes, LDA+U (Anisimov et al., 1991) is the most practical method for minerals under the current state of computer technology. The main problem of applying LDA+U to materials under pressure is the determination of the effective Hubbard U parameter, meaning screened on-site Coulomb interaction. Tsuchiya et al. (2006), Hsu et al. (2011), and Metsue and Tsuchiya (2011) computed the effective U in magnesiowüstite (Mw) ($\text{Mg}_{1-x}\text{Fe}_x\text{O}$), perovskite ($\text{Mg}_{0.875}\text{Fe}_{0.125}^{3+}$)($\text{Si}_{0.875}\text{Fe}_{0.125}^{3+}\text{O}_3$), and PPv ($\text{Mg}_{0.9375}\text{Fe}_{0.0625}\text{SiO}_3$) in a nonempirical and internally consistent way based on a linear response approach for the occupancy matrix (Cococcioni and de Gironcoli, 2005), respectively.

Combining these techniques, the ab initio lattice dynamics method (Baroni et al., 1987, 2001) and quasiharmonic approximation (Wallace, 1972), the calculation condition was successfully extended to finite temperature including phonon thermodynamics (Karki et al., 2000a,b; Tsuchiya, 2003; Tsuchiya et al., 2004a,c). EoS and other high-temperature properties can now be computed in the whole mantle P , T condition quite accurately, even nonempirically. The density functional perturbation theory (Baroni et al., 1987, 2001) plays a key role there, allowing direct access to the harmonic dynamical matrix. More recently, the technique was further extended to high-temperature properties of iron-bearing systems combined with the internally consistent LDA+U (Fukui et al., 2012; Metsue and Tsuchiya, 2011, 2012; Tsuchiya and Wang, 2013).

Another important new research direction is a technical enhancement in evaluating transport properties. For example, an extension of the harmonic lattice dynamics framework to the anharmonic lattice dynamics enabled access to lattice thermal conductivity of minerals, which is important in understanding the deep mantle thermal property. Dekura et al. (2013) calculated lattice thermal conductivity of MgSiO_3 perovskite under the lower mantle P , T conditions for the first time within the third-order level of anharmonicity, and estimated a moderate core–mantle boundary (CMB) heat flow of ~ 3 – 6 TW and a Rayleigh number of the lower mantle large enough to drive a vigorous convection. Metsue and Tsuchiya (2013), on the other hand, investigated the shear response of possible slip systems activated in Fe-bearing MgSiO_3 PPv based on generalized stacking fault (GSF) energy calculations. Although some computational conditions such as system size or chemical composition are limited in these studies compared to actual systems, this situation will be greatly improved in the near future.

2.03.2.3 Pressure Scale

The construction of an accurate pressure standard is a critical issue in the quantitative measurements of mineral physics properties under high pressure. The pressure (P)–volume (V)–temperature (T) EoS (PVT-EoS) of materials is most useful in evaluating the experimental pressures under the P , T conditions of the Earth's deep mantle. The EoS of a pressure standard is usually derived on the basis of a conversion of dynamical shock Hugoniot data to isothermal compression data. In principle, some parameters specifying the thermal properties of a solid are necessary for this conversion process of the Hugoniot. However, measurements of these parameters without any pressure or temperature standards are virtually impossible. In all EoSs presently used as primary pressure standards, the conversion of the Hugoniot was, therefore, performed with some simple assumptions about the unknown high-pressure behavior of the conversion parameters. The most critical issue on the validity of such assumptions is the volume dependence of the thermodynamic Grüneisen parameter, which is a fundamental quantity characterizing the thermal effect on the material.

The characteristic properties of gold (Au), namely its low rigidity, simple crystal structure, chemical inertness, and structural stability, make it particularly suitable as a pressure standard under high P , T conditions, and it has, therefore, been used as a primary standard in many in situ x-ray diffraction studies (e.g., Funamori et al., 1996; Mao et al., 1991). However, some recent in situ experiments noted that the pressure values estimated by different thermal EoSs of gold show significant discrepancies. Using the EoS of gold proposed by Anderson et al. (1989), which is frequently used as the pressure scale in experiments using multianvil apparatus, Irifune et al. (1998a) first reported that the postspinel phase boundary of Mg_2SiO_4 shifted to about 2.5 GPa lower than the pressure corresponding to the depth of the 660-km seismic discontinuity (~ 23.5 GPa and ~ 2000 K). Similar results were obtained for other various minerals as summarized in Irifune (2002).

Tsuchiya (2003) predicted the thermal properties and the PVT-EoS of gold based on the ab initio theory including thermal effect of electrons. The state-of-the-art ab initio calculation showed that the relationship $\gamma/\gamma_0 = (V/V_0)^q$, assumed in some studies, is adequate for gold, at least up to $V/V_0 = 0.7$ and the predicted values of q was 2.15, which is intermediate between the values used in Heinz and Jeanloz (1984) and Anderson et al. (1989). According to this study, the ab initio EoS model reduced the discrepancies between the observed phase boundaries of spinel, ilmenite, and garnet and the seismic discontinuity. However, a gap of about 0.7 GPa still remains between the postspinel transition pressure and that of the 660-km discontinuity. The similar conclusions with a slightly larger (1.0–1.4 GPa) discrepancy has also been obtained by an experimental study using an empirical PVT-EoS model of MgO to determine pressure (Matsui and Nishiyama, 2002).

Even for gold, there are several PVT models, derived by different groups, which are still not mutually consistent. Such a problem is also found in EoSs of platinum (Holmes et al., 1989; Jamieson et al., 1982). Moreover, platinum appears to be unsuitable for the pressure scale in some cases because of its reactivity with the sample or materials of the experimental cell at high P , T conditions (Ono et al., 2005a). A similar problem

is also encountered with the pressures obtained using MgO. The pressures obtained using EoSs of different materials, therefore, show a significant scatter. Akahama et al. (2002) determined the pressures based on room-temperature EoSs of several materials compressed simultaneously in a diamond anvil cell and reported that the EoS of platinum proposed by Holmes et al. (1989) provided pressures more than 10 GPa higher than those calculated using EoS of gold as proposed by Anderson et al. (1989) at pressures of a megabar even at 300 K. A similar inconsistency has also been reported in pressure determination based on gold and silver EoSs (Akahama et al., 2004).

Examples of the difference in pressures based on a different EoS of gold than that of platinum are shown in Figure 1, along a temperature (2300 K) close to the typical lower mantle geotherm. The pressures evaluated based on various EoSs of gold differ by $\sim 2\text{--}3$ GPa at the pressures of the uppermost parts of the lower mantle (25–30 GPa), and are within 5 GPa at pressures up to ~ 60 GPa. However, the differences become substantially larger at higher pressures, reaching ~ 15 GPa at the base of the lower mantle (136 GPa). It is also seen that the pressures based on an EoS of Pt (Holmes et al., 1989) are even higher than the highest pressure estimation by Tsuchiya (2003) by 5 GPa at 136 GPa.

An attempt to determine a more accurate and reliable EoS of MgO was made by using unified analyses for available pressure-scale-free experimental data sets, including shock-compression Hugoniot, zero-pressure thermal expansion, high-temperature adiabatic bulk moduli, and room-temperature and high-pressure adiabatic bulk moduli data (Tange et al., 2009a). The resultant EoS successfully reproduced all the data used for the analyses throughout the entire lower mantle P , T conditions, which yields slightly higher pressures than those derived by other EoSs of MgO commonly used for in situ x-ray measurements (Matsui et al., 2000; Speziale et al., 2001). The new EoS of MgO yields the spinel–postspinel transition pressure of about 22.5 GPa at 2000 K (Tange et al., 2009a) using the experimental data of Fei et al. (2004), which is about 1 GPa lower than the pressure for the

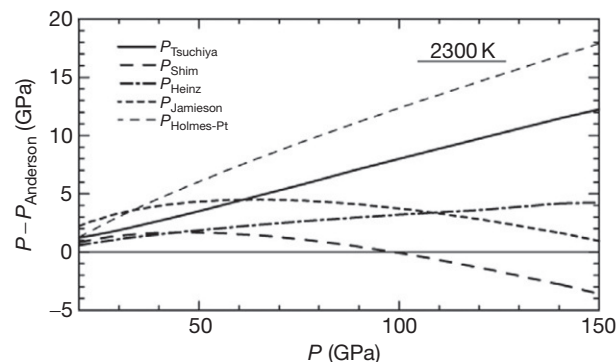


Figure 1 Differences between the pressures calculated using various equation of states (EoSs) of gold (Heinz and Jeanloz, 1984; Jamieson et al., 1982; Shim et al., 2002a; Tsuchiya, 2003) and those based on Anderson et al. (1989, horizontal line) as a function of pressure at 2300 K. The difference between the pressures using the Anderson scale and those using EoS of platinum by Holmes et al. (1989) is also shown for comparison.

660 km discontinuity. A pressure-scale-free EoS of MgO has also been proposed on the basis of the analyses of ultrasonic sound velocity data combined with unit-cell volume compression data (Kono et al., 2010), which yields pressures consistent with those derived by the above pressure scale at least at pressures to the upper parts of the lower mantle.

2.03.3 Mineral Phase Transitions in the Lower Mantle

2.03.3.1 Major Minerals in the Mantle and Subducted Slab

Phase transitions in Earth-forming materials dominate the structure and dynamics of the Earth. Major changes in seismic velocities traveling through the Earth's mantle can be generally attributed to the phase transitions of the constituent minerals, although some of them may be closely related to some chemical changes. Exploration and investigation of high-pressure phase transitions in mantle minerals have, therefore, been one of the major issues in studying the Earth's deep interior.

Here, we summarize the phase transitions in major minerals under lower mantle conditions. Phase transitions in some relatively minor minerals relevant to the subducted slab lithologies are also reviewed in the following section. As the experimental data on the phase transitions are still limited and controversial at P , T conditions of the lower mantle, we have tried to construct the most likely phase diagrams for the minerals with simple chemical compositions based on available laboratory data and ab initio calculations. Thermoelastic properties of some key high-pressure phases are also reviewed and summarized here, as far as experimental data or theoretical predictions are available.

2.03.3.1.1 MgSiO_3

The high-pressure orthorhombic perovskite polymorph of MgSiO_3 (Mg-Pv) is believed to be the most abundant mineral in the Earth's lower mantle. The possibility of a further phase transition of this phase under the lower mantle P , T conditions has been controversial: Some studies suggest that Mg-Pv dissociates into an assemblage of SiO_2 and MgO at 70–80 GPa and 3000 K (Meade et al., 1995; Saxena et al., 1996) or that it undergoes a subtle phase change above 83 GPa and 1700 K (Shim et al., 2001b), while others claimed Mg-Pv is stable almost throughout the lower mantle (e.g., Fiquet et al., 2000). However, more recent studies suggest that the result of Shim et al. (2001b) was due to misidentification of the diffraction peaks of a newly formed platinum carbide (Ono et al., 2005a). The dissociation of Mg-Pv into the oxides is also unlikely to occur in the Earth's mantle according to the subsequent experimental (Murakami et al., 2004a, 2005; Oganov and Ono, 2004) studies. Theoretical investigations also suggest the dissociation should occur at extremely high pressure above 1 TPa (Tsuchiya and Tsuchiya, 2011b; Umemoto et al., 2006).

Recently, the Pv to PPv transition in MgSiO_3 was found to occur by in situ x-ray diffraction experiment using LHDAC and ab initio calculations at ~ 2500 K and ~ 125 GPa (Murakami et al., 2004a; Oganov and Ono, 2004; Tsuchiya et al., 2004a; Figure 2), close to the P , T conditions of the D'' layer near the CMB. The Mg-PPv phase has a crystal structure identical to that of CaIrO_3 with a space group Cmcm . This structure consists of

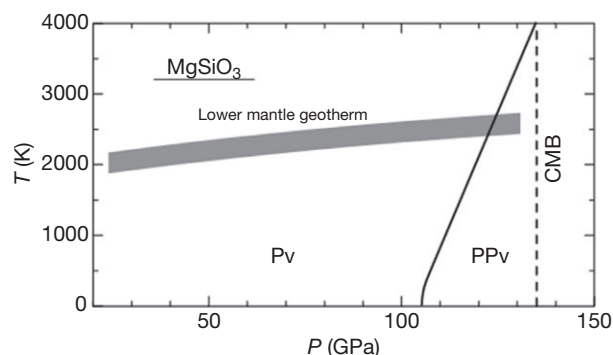


Figure 2 High P , T phase diagram for MgSiO_3 at lower mantle pressures summarized based on the laser-heated diamond anvil cell (LHDAC) experiments by Murakami et al. (2004a) and ab initio calculations by Tsuchiya et al. (2004a). Shaded area represents a typical lower mantle geotherm based on Brown and Shankland (1981). Pv, perovskite; PPv, postperovskite; CMB, core–mantle boundary.

silica layers stacking along the b direction and intercalated Mg ions. In the silica layers, SiO_6 octahedra connect sharing edges along the a direction and sharing corners along the c direction. Thus, this structure is more favorable at high pressure than the Pv structure, although the cation coordinations are basically the same in both structures.

The PPv structure is expected to be highly anisotropic. It is more compressible along the b direction perpendicular to the silica layers because only ionic Mg–O bonding exists in the interlayer spacing. The Pv and PPv structures, therefore, look very different in this respect. However, the structural relationship between Pv and PPv is quite simple and by applying shear strain ϵ_6 , Pv can change to PPv directly (Tsuchiya et al., 2004a). According to this relation, the c direction remains unchanged via the structural transition. This suggests that nonhydrostaticity could significantly affect the transition kinetics of the Pv to PPv transition.

PPv's thermodynamic properties and the position and slope of the phase boundary were investigated by means of ab initio quasiharmonic free energy calculations (Tsuchiya et al., 2004a, 2005b). The predicted Clapeyron slope of the Pv–PPv transition was $\sim 7.5 \text{ MPa K}^{-1}$, which is remarkably close to that required for a solid–solid transition to account for the D'' discontinuity (Sidorin et al., 1999). Thus, the results of both experimental and theoretical studies suggest that the PPv should be the most abundant high-pressure phase in the D'' region.

Over the past decades, there have been a number of experiments to determine the elastic property of Mg–Pv (e.g., Fiquet et al., 2000; Funamori et al., 1996; Mao et al., 1991; Ross and Hazen, 1990; Yagi et al., 1982; Yeganeh-Haeri et al., 1989). Among these experiments, early studies yielded relatively large variations for zero-pressure bulk modulus K_0 of Mg–Pv ranging from 254 (Ross and Hazen, 1990) to 273 GPa (Mao et al., 1991). However, more recent experiments of static compression and Brillouin spectroscopy yielded mutually consistent K_0 values of ~ 253 – 264 GPa. Density functional calculations have reported similar but slightly smaller room-temperature bulk modulus for Mg–Pv of about 250 GPa (Tsuchiya et al., 2004b, 2005b; Wentzcovitch et al., 2004). This underbinding

tendency for Mg–Pv is seen in standard DFT calculations but is much more prominent in GGA than in LDA (Wentzcovitch et al., 2004).

In contrast to the extensive investigations of the EoS of Mg–Pv, the EoS of Mg–PPv has not been well constrained experimentally. According to a density functional prediction, the zero-pressure volume of Mg–PPv is very close to that of Mg–Pv (Tsuchiya et al., 2004a, 2005b). However, K_0 and its pressure derivative of Mg–PPv are significantly smaller and larger than those of Mg–Pv, respectively, which implies the volume of Mg–PPv should be smaller than that of Mg–Pv at the relevant pressure range. The volume decrease associated with the Pv–PPv transition is estimated to be $\sim 1.5\%$ on the basis of ab initio calculations (Tsuchiya et al., 2004a), which is consistent with those estimated based on LHDAC experiments.

2.03.3.1.2 MgSiO_3 – FeSiO_3

Mg–Pv is supposed to incorporate 5–10 mol% of FeSiO_3 in peridotitic compositions in the lower mantle (Irfune, 1994; Katsura and Ito, 1996; Wood and Rubie, 1996). However, experimental studies for the system MgSiO_3 – FeSiO_3 have been limited to the pressures of the uppermost part of the lower mantle, except for a LHDAC study (Mao et al., 1991). Recent developments in KMA with sintered diamond anvils substantially extend the pressure and temperature ranges for phase equilibrium studies as reviewed earlier, and Tange et al. (2009b) extensively studied the phase relations and the Mg–Fe partitioning between coexisting Mg–Pv and Mw at pressures up to ~ 50 GPa and temperatures to 2300 K.

Immediately after the discovery of the Pv–PPv transition in MgSiO_3 , the effects of iron on this transition were studied using LHDAC (Mao et al., 2004, 2005). It was noted that the presence of iron significantly reduce the stability pressure of PPv, and PPv with up to ~ 80 mol% of the FeSiO_3 component synthesized at a pressure of ~ 140 GPa and at temperatures of ~ 2000 K (Mao et al., 2005). However, subsequent studies (Andrault et al., 2010; Hirose et al., 2008; Sinmyo et al., 2008; Stixrude and Lithgow-Bertelloni, 2011; Tateno et al., 2007) suggest that the presence of ferrous iron increases the stability pressure of PPv, contrary to this study. Thus, the phase relations in the system MgSiO_3 – FeSiO_3 at pressure up to ~ 130 GPa and at a typical lower mantle temperature can be drawn as illustrated in Figure 3, according to the results of these more recent studies, although the phase boundaries at pressures higher than 50 GPa have not been well constrained.

A large Pv+PPv coexisting pressure range of ~ 20 GPa was observed for the $(\text{Mg}_{0.9}\text{Fe}_{0.1})\text{SiO}_3$ composition (Catalli et al., 2009), but the multicomponent phase boundary determined by the LHDAC technique in the Mbar condition suffers substantial uncertainty. On the other hand, a significant effect of ferrous iron on the stability of Mg–PPv has also been predicted by some theoretical works using GGA (Caracas and Cohen, 2005b; Stackhouse et al., 2006). However, this technique is known to be less applicable to the iron-bearing system as mentioned earlier. In contrast, a recent internally consistent LDA+U+ab initio LD+QHA study showed much smaller effects even at mantle temperatures (Metsue and Tsuchiya, 2012), being consistent with a different LHDAC experiment (Sinmyo et al., 2008). These calculations, particularly Tsuchiya and Wang (2013), also reported that a Pv dominant

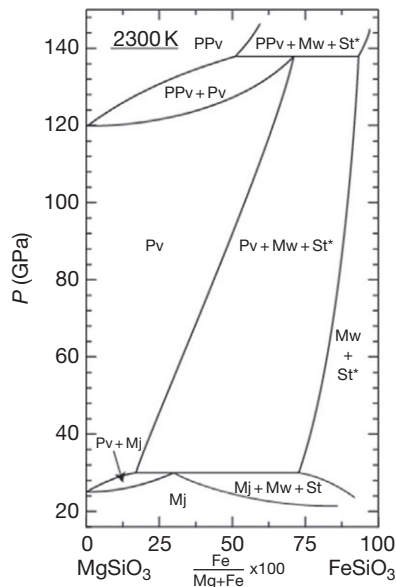


Figure 3 A predicted phase diagram for the system $\text{MgSiO}_3\text{--FeSiO}_3$ at lower mantle pressures and at a representative lower mantle temperature (2300 K). The relations below ~ 30 GPa are estimated on the basis of Sawamoto (1987) and Ohtani et al. (1991) using Kawai-type multianvil apparatus (KMA), while those above 80 GPa are based on LHDAC experiments by Tatenko et al. (2007) and Hirose et al. (2008) but may suffer substantial uncertainties in the phase boundaries. The boundaries between these pressures are depicted based on recent experimental data using KMA with SD anvils (Tange, 2009a). Mj, majorite garnet; Mw, magnesiowüstite; St, stishovite; *stishovite, CaCl_2 -type or $\alpha\text{-PbO}_2$ -type phases, depending on pressure.

composition cannot reproduce seismological observations of the lower mantle. This is qualitatively consistent with an EoS measurement of Pv (Tange et al., 2012), but less supportive of a Brillouin scattering experiment (Murakami et al., 2012).

The effect of iron on the PPv transition has also been studied in the light of the high-pressure phase changes of hematite, corundum-type Fe_2O_3 . Hematite transforms first to the high-pressure phase with the $P6_{3/m}$ Pv structure or $\text{Rh}_2\text{O}_3(\text{II})$ structures at 30 GPa, whose x-ray diffraction patterns are very similar to each other (Ono et al., 2005b). Further transitions in Fe_2O_3 to the structure assigned as the CaIrO_3 -type structure has been reported to occur at a transition pressure of ~ 50 GPa (Ono et al., 2005b). This transition pressure is significantly lower than the Pv–PPv transition pressure in MgSiO_3 . Thus, the presence of iron in the trivalent state is also suggested to lower the pressure of the Pv–PPv transition, unlike divalent ferrous iron. Nevertheless, this issue has not been fully resolved and there remains a lot of room for further theoretical and experimental investigation.

2.03.3.1.3 $\text{MgSiO}_3\text{--Al}_2\text{O}_3$

Irfune (1994) demonstrated that Mg–Pv is the major host of aluminum in a pyrope composition at pressures and temperatures of the uppermost parts of the lower mantle, possessing ~ 4 mol% of Al_2O_3 . Phase relations in the system $\text{MgSiO}_3\text{--Al}_2\text{O}_3$ under the lower mantle conditions have since been studied (Irfune et al., 1996a; Ito et al., 1998) with an emphasis on the $\text{MgSiO}_3\text{--Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ system. Irfune et al.

(1996a) showed that majorite garnet with less than ~ 15 mol% Al_2O_3 transforms to the Pv structure via a mixture of these two phases, while this assemblage further changes to an assemblage of majorite plus corundum at pressures about ~ 28 GPa, at 1800 K. This assemblage with the $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ composition was later shown to form almost pure Pv at ~ 38 GPa using KMA with SD anvils (Ito et al., 1998).

Phase transitions in Al_2O_3 corundum under the lower mantle condition were first studied by Funamori and Jeanloz (1997) using LHDAC based on earlier ab initio predictions (Marton and Cohen, 1994; Thomson et al., 1996), which demonstrated that corundum transforms to a new phase with the $\text{Rh}_2\text{O}_3(\text{II})$ structure at ~ 100 GPa and at ~ 1000 K. More recently, it has been predicted by ab initio studies that Al_2O_3 has a similar high-pressure phase relation to Fe_2O_3 (Caracas and Cohen, 2005a; Stackhouse et al., 2005b; Tsuchiya et al., 2005c). The Pv to PPv transition was thus suggested to occur in Al_2O_3 at about 110 GPa at 0 K, although the Pv phase is eclipsed by the stability field of the $\text{Rh}_2\text{O}_3(\text{II})$ phase. This Pv to PPv transition pressure in Al_2O_3 is about 10 GPa higher but fairly close to that in MgSiO_3 , though Akber-Knutson et al. (2005) predicted a much larger effect of Al by estimating the solid solution energy. In contrast to these static-temperature calculations, a more careful modeling for finite temperature, solid-solution phase equilibria based on the statistical mechanical multi-configuration sampling approach (Tsuchiya and Tsuchiya, 2008) indicated a much smaller effect of aluminum. A narrow Pv+PPv coexisting pressure width expected for the reasonable Al content in the lower mantle could be responsible for the observations of the sharp D'' discontinuity (Lay et al., 1998).

In situ x-ray diffraction experiments on pyrope compositions by LHDAC (Tatenko et al., 2005) demonstrated a consistent result regarding the effect of aluminum incorporation on the PPv transition pressure. Andrault et al. (2010) also reported a large Pv+PPv coexisting region from ~ 120 to ~ 150 GPa in the peridotitic Al and Fe composition and from ~ 100 to ~ 180 GPa in a more felsic composition by LHDAC. The broad coexisting region was similarly observed by LHDAC (Catalli et al., 2009; Nishio-Hamane et al., 2007), although the pressure intervals of the coexisting regions are inconsistent in these studies. For instance, Nishio-Hamane et al. (2007) reported that the coexisting region starts from ~ 150 GPa and ends at ~ 170 GPa in the similar composition, which is substantially higher than those of other studies and even higher than the CMB pressure (136 GPa). These conflicting results show that the accurate determination of the multicomponent phase boundary is difficult for the Mbar region using current LHDAC techniques. Thus, we rely on the theoretical results and expect that the effect of aluminum on the PPv transition pressure in MgSiO_3 is not very significant. The plausible phase diagram of the system $\text{MgSiO}_3\text{--Al}_2\text{O}_3$ in the lower-mantle P , T condition is illustrated in Figure 4.

The presence of Al_2O_3 in Fe-bearing Pv is known to lead to a coupled substitution of Fe^{3+} and Al^{3+} for Mg^{2+} and Si^{4+} in Pv (Frost and Langenhorst, 2002; McCammon, 1997; Wood and Rubie, 1996), yielding substantial enrichment of ferric iron in Pv in the uppermost regions of the lower mantle (Irfune, 1994; Irfune et al., 2010; Nishiyama and Yagi, 2003; Wood, 2000). In addition to this coupled substitution effect, it has

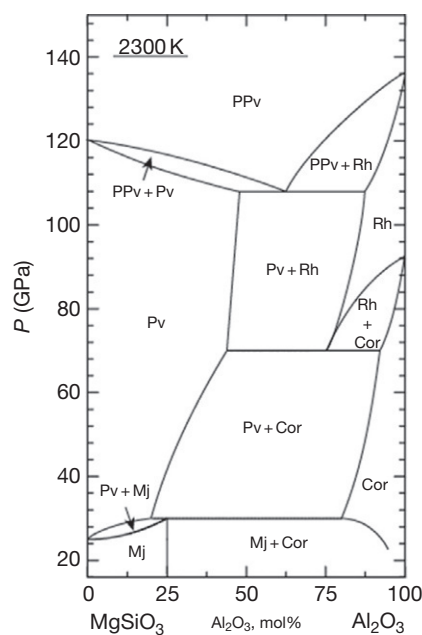


Figure 4 A predicted phase diagram for the system $\text{MgSiO}_3\text{--Al}_2\text{O}_3$ at lower mantle pressures and at 2300 K. The phase relations below ~ 40 GPa are based on KMA experiments (Irifune et al., 1996a; Ito et al., 1998), while those on Al_2O_3 are from Funamori et al. (1998) using LHDAC and ab initio calculations by Tsuchiya et al. (2005c). The boundaries at 120–130 GPa are based on a theoretical prediction by Tsuchiya and Tsuchiya (2008). Cor, corundum; Rh, $\text{Rh}_2\text{O}_3(\text{II})$.

been suggested that the high-spin to low-spin transitions in both Pv and Mw may cause some significant changes in the partitioning of iron between these major phases in the lower mantle. Although the nature of the spin transition in Mw has been fairly well understood based on recent ab initio computations and experimental studies (see below), those in Pv have not yet been resolved. This is partly because Pv has two cation sites (A and B) and can accommodate both ferrous and ferric irons, depending on the alumina content, which makes the computational and experimental studies extremely difficult. The current situations on the studies of spin transitions in Pv can be seen in a recent comprehensive review article (Lin et al., 2013), which, however, may suffer some significant revisions in the near future, considering the rapid progress in this research field.

2.03.3.1.4 MgO–FeO

Mw, $(\text{Mg}_{1-x}\text{Fe}_x)\text{O}$, is believed to be the next major mineral phase in Earth's lower mantle after ferrosilicate Pv ($\text{Mg}_{1-x}\text{Fe}_x\text{SiO}_3$ (e.g., Helffrich and Wood, 2001). The magnesium end-member of Mw, periclase, possessing the B1 (NaCl) structure, is known to be an extraordinarily stable phase. No phase transitions in this material have been observed or predicted under the P, T conditions of the entire mantle (Alfé et al., 2005; Duffy et al., 1995), primarily due to substantially smaller ionic radius of magnesium relative to that of oxygen. FeO wüstite, on the other hand, transforms to an antiferromagnetic phase accompanied by a small rhombohedral distortion. This transition is a typical magnetic order–disorder transition and, therefore, the transition temperature corresponds to the Neel

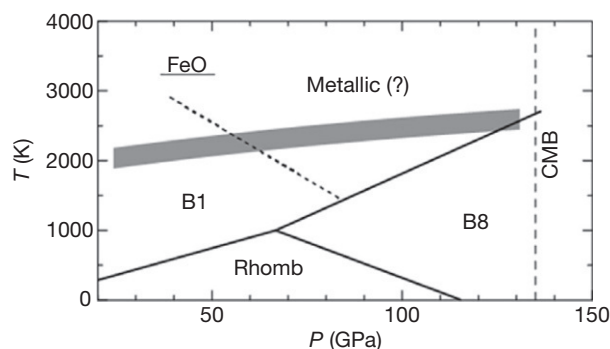


Figure 5 High P, T phase diagram for FeO at lower mantle pressures summarized based on the in situ measurement by Fei and Mao (1994), Murakami et al. (2004b), and Kondo et al. (2004). The P, T boundary above which metallization in FeO is reported to occur (Ohta et al., 2012) is shown by the dotted line. B1, NaCl structure; B8, NiAs structure; Rhomb, rhombohedral B1 phase.

point. Although the rhombohedral B1 (rB1) phase is stable at low temperatures up to about 110 GPa, at higher pressure over 65 GPa and high temperatures, the rB1 phase transforms to the normal or inverse B8 (NiAs) structure, as shown in Figure 5 (Fei and Mao, 1994; Kondo et al., 2004; Murakami et al., 2004b). However, several important properties of this high-pressure phase, such as high-temperature stability, structural details, and electronic property, are still in debate (Fei and Mao, 1994; Mazin et al., 1998; Murakami et al., 2004b).

For the compositions between the two end-members of MgO and FeO, some controversial experimental results have emerged: Mw with $X_{\text{Fe}}=50\%$ was reported to dissociate into two components, Fe-rich and Mg-rich Mws at 86 GPa and 1000 K (Dubrovinsky et al., 2000). In contrast, another study using LHDAC found no dissociation of Mw with even higher X_{Fe} of 61% and 75% up to 102 GPa and 2550 K, though the sample with $X_{\text{Fe}}=75\%$ showed a displacive transition to the rB1 structure at low temperature similar to FeO wüstite (Lin et al., 2003). Thus, further experimental and theoretical studies are required to address the possible dissociation of Mw.

It has been demonstrated that FeO with the B1 structure suffers metallization under the P, T conditions of the lower mantle (Figure 5) on the basis of electric conductivity (Ohta et al., 2010, 2012) and radiometric (Fischer et al., 2011) measurements, as well as first principles calculations (Ohta et al., 2012). Metallization of FeO suggests that oxygen may be readily incorporated into the Earth's core as the major alloying light element with some important geochemical implications (Ringwood et al., 1990). Moreover, the possible existence of the iron-rich Mw in the lowermost mantle (e.g., Wicks et al., 2010) should lead to strong electromagnetic interactions with the liquid outer core if such Mw is of metallic nature.

Another issue relevant to Mw, as well as the ferrosilicate Pv, which should affect the thermoelastic properties of these phases, is the occurrence of electron spin transitions under the lower mantle conditions. High spin (HS) to low spin (LS) transitions in iron have been observed by in situ x-ray emission spectroscopy and Mössbauer spectroscopy from 40 to 70 GPa in Mw containing about 18% iron (Badro et al., 2003; Lin et al., 2005) and from 70 to 120 GPa in $(\text{Mg,Fe})\text{SiO}_3$ Pv

(Badro et al., 2004; Jackson et al., 2005; Li et al., 2004) at room temperature. Several significant effects of the thermochemical state of the lower mantle can be inferred by the spin transition of iron. The spin transition in Mw is accompanied by significant volume reductions (Lin et al., 2005; Tsuchiya et al., 2006) and changes in these minerals' optical absorption spectrum (Badro et al., 2004). These can produce (1) seismic velocity anomalies, (2) variations in Mg-Fe²⁺ partitioning between Mw and Pv, (3) changes in radiative heat conductivity, and (4) compositional layering (Badro et al., 2003, 2004; Gaffney and Anderson, 1973). The elastic signature of this transition in Mw has been partially explored (Lin et al., 2005), but there is still much uncertainty. In contrast, anomalous compression behavior has not yet been observed in (Mg,Fe)SiO₃ Pv.

The strongly correlated behavior of iron oxide has deterred the quantification of these changes by density functional calculations based on the local spin density approximation and spin polarized generalized gradient approximation (σ -GGA). These approaches incorrectly predict a metallic HS ground state and then successive spin collapses across the transition as reported for FeO (Cohen et al., 1997; Sherman and Jansen, 1995). More recently, a new model explaining the mechanism of HS-to-LS transition of iron in Mw has been proposed based on calculations using a more sophisticated LDA+U technique that describes the electronic structure of a strongly correlated system more correctly (Tsuchiya et al., 2006). In this study, the effective Hubbard U parameter has been optimized at each volume and at each iron concentration up to X_{Fe} of 18.75% in an internally consistent way. As a result, it has been demonstrated that the large stability field of HS/LS mixed state appears at high temperatures instead of the intermediate spin state, due to the contributions of coexisting HS/LS mixing entropy and magnetic entropy. According to this transition mechanism, Mw is expected to be in this HS/LS mixed state for almost the entire range of lower mantle P , T conditions with the proportion of HS iron decreasing continuously with increasing pressure (Figure 6). No discontinuous change in any physical properties would appear to be associated with the spin transition in Mw within this range. Although phonon effects were neglected to calculate the high-temperature energetics in Tsuchiya et al. (2006), these effects were later examined by the internally consistent LDA+U+ab initio LD+QHA

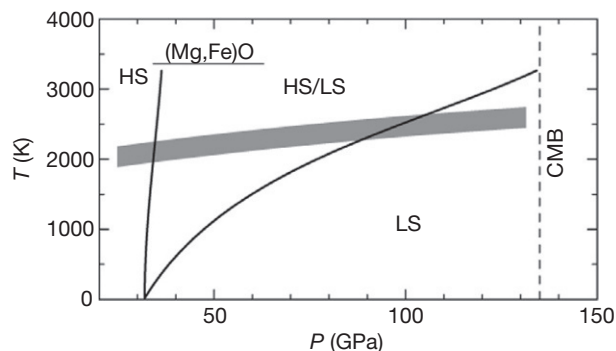


Figure 6 High P , T spin transition diagram for Mw with iron concentration of 18.75% at lower mantle pressures predicted on the basis of LDA+U calculations by Tsuchiya et al. (2006). HS, high spin; LS, low spin.

calculations (Fukui et al., 2012), which demonstrated that the effects are indeed unchanged across the spin transition and thus negligible in calculating the finite-temperature mixed spin (MS) region at least for the (Mg_{0.875}Fe_{0.125})O composition.

It has been reported that the spin transition pressure significantly increases with increasing X_{Fe} . A volume decrease associated with the spin transition was observed in (Mg_{0.4}Fe_{0.6})O at 95 GPa (Lin et al., 2005), while no spin transition has so far been reported in pure FeO up to 143 GPa (Badro et al., 1999). Iron-iron interactions, which are no longer negligible at X_{Fe} higher than 20%, might also reinforce the magnetic moment significantly, although the mechanism of this tendency has not been fully understood to date.

Some studies propose anomalous behaviors in the MS state of Mw for elasticity (Crowhurst et al., 2008; Marquardt et al., 2009a; Wentzcovitch et al., 2009), electrical conductivity (Lin et al., 2007), and viscosity (Wentzcovitch et al., 2009). These, however, currently lack corroborative evidence. In contrast, other experiments observed no, or marginal, anomalies in the elasticity of Mw (Antonangeli et al., 2011; Murakami and Bass, 2011). Although further investigations are clearly required for detailed understanding, the latter seems physically reasonable if the MS state is considered to be a kind of two-phase coexistence.

It is also pointed out that the spin crossover in Mw affects its elastic anisotropy (Marquardt et al., 2009b). LS Mw was reported to have at least 50% stronger shear anisotropy in the lowermost mantle compared to MgO, which is originally quite anisotropic at high pressures (Karki et al., 1999; Tsuchiya and Kawamura, 2001). According to this result, Mw was inferred to be a dominant cause of seismic anisotropy in the D'' layer (Marquardt et al., 2009b), but careful modeling of the rheological property, including both PPv and Mw, is obviously required to analyze the source of observed anisotropy in more detail (Merkel et al., 2007; Metsue and Tsuchiya, 2013; Miyagi et al., 2010).

2.03.3.1.5 CaSiO₃

The lower mantle is believed to consist mainly of (Mg,Fe)SiO₃ Pv and Mw, with some CaSiO₃ perovskite (Ca-Pv) up to 7–8 vol% (e.g., Irifune, 1994). Despite its importance, there are many unanswered questions about the structure, stability, EoS, and other physical properties of Ca-Pv under pressure and temperature, which complicate some attempts to model the mineralogy of the lower mantle (e.g., Stacey and Isaak, 2001).

CaSiO₃ crystallizes to the Pv structure over 10–13 GPa, depending on temperature, and is known to be unquenchable at ambient conditions. At lower mantle conditions, CaSiO₃ has an ideal cubic Pv structure, while, at lower temperatures, it is suggested to be slightly distorted. The small degree of the possible distortion is hardly observed by current high-temperature and high-pressure x-ray techniques, and several orthorhombic and tetragonal structures have been proposed, based on in situ x-ray diffraction measurements (Kurashina et al., 2004; Ono et al., 2004; Shim et al., 2002b) or theoretical calculations (Caracas et al., 2005; Chizmeshya et al., 1996; Magyari-Köpe et al., 2002; Stixrude et al., 1996).

EoS of Ca-Pv has been determined up to CMB pressures by different groups (e.g., Kurashina et al., 2004; Mao et al., 1989;

Ono et al., 2004; Shieh et al., 2004; Shim et al., 2000a,b, 2002b; Tamai and Yagi, 1989; Wang et al., 1996). The fitting of the experimental results by third-order Birch–Murnaghan EoS, yielded a unit-cell volume, $V_0 = 45.54 \text{ \AA}^3$, bulk modulus, K_0 , ranging from 232 to 288 GPa, and its pressure derivative, K'_0 , within 3.9–4.5. Most of the recent results, with careful removing of the effect of deviatoric stress on the produced pressure, however, yielded the lower end values (232–236 GPa; Wang et al., 1996; Shim et al., 2000b) in this range. The results of corresponding ab initio studies (e.g., Chizmeshya et al., 1996; Karki and Crain, 1998; Stixrude et al., 1996; Wentzcovitch et al., 1995) are similar to those obtained for the experimental data. Most of these studies, both experimental and theoretical, have focused on the behavior of the cubic modification of CaSiO_3 under pressure.

Caracas et al. (2005) performed a detailed investigation of the major symmetry-allowed modifications of CaSiO_3 obtained as distortions from the parent cubic phase by means of ab initio pseudopotential theory. They examined nine modifications having different symmetries and reported that the I4/mcm phase is the most likely stable static atomic configuration up to about 165 GPa. Enthalpy difference between this I4/mcm and the cubic Pv phase increased with increasing pressure, indicating that the I4/mcm structure becomes more stable relative to the cubic structure at higher pressure. The bulk modulus was estimated to be about 250 GPa for all modifications with the exception of the R-3c structure. This theoretical K_0 is fairly similar to recent experimental values (Shim et al., 2002b; Wang et al., 1996), but much smaller than those reported in earlier nonhydrostatic experiments (Mao et al., 1989; Tamai and Yagi, 1989).

Some studies focused on the high-temperature phase change from low symmetry phase to cubic Ca-Pv. Ono et al. (2004) reported that this transition occurs at about 600–1200 K at 25–120 GPa, where the transition temperature increased with increasing pressure, consistent with the theoretical prediction (Caracas et al., 2005). These temperatures are much lower than the typical lower mantle geotherm of about 2000–2500 K, suggesting that CaSiO_3 may have the cubic form throughout the actual lower mantle (Figure 7). However, most recent ab initio molecular dynamics studies (Li et al., 2006a,b) reported very different results. They found the tetragonal phase stable even at the mantle temperatures in addition to the low-

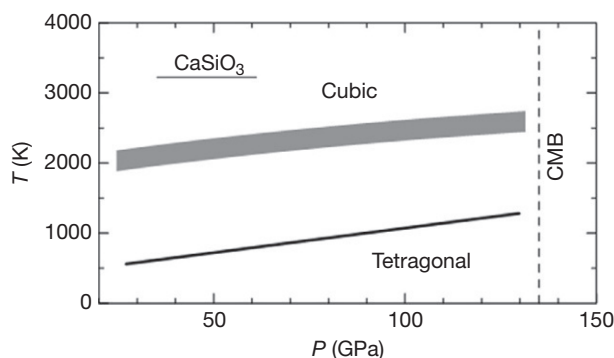


Figure 7 High P , T phase diagram for CaSiO_3 at lower mantle pressures summarized based on the LHDAC experiments by Kurashina et al. (2004) and Ono et al. (2004).

temperature stability of the orthorhombic phase. Their calculated elasticity of Ca-Pv is also very different from earlier results (Karki and Crain, 1998) particularly with respect to the shear modulus. The cause of the discrepancies is explained by Tsuchiya (2011), who advocates that even cubic Ca-Pv should have a smaller shear modulus comparable to that of tetragonal Ca-Pv.

2.03.3.1.6 SiO_2

Recent theoretical studies suggest that a second-order displacive phase transition from stishovite (St) to the CaCl_2 -type structure occurs at 50–60 GPa at room temperature (Kingma et al., 1995). It has also been predicted that the CaCl_2 -type silica undergoes a further structural transition to the α - PbO_2 phase (Dubrovinsky et al., 1997; Karki et al., 1997a). The results of the experimental studies on these issues, however, have been controversial. LHDAC studies reported that the CaCl_2 -type phase persists at least up to 120 GPa (Andrault et al., 1998), and the transition to the α - PbO_2 phase occurs at 121 GPa and 2400 K (Murakami et al., 2003). In contrast, another similar experiment showed that the α - PbO_2 -like phase was formed from cristobalite above 37 GPa at room temperature, and that St directly transformed to the α - PbO_2 -type structure above 64 GPa at 2500 K with a negative Clapeyron slope (Dubrovinsky et al., 2001). In addition, Sharp et al. (1999) found the α - PbO_2 -type phase in a natural meteorite sample, which would have experienced very low shock pressure below 30 GPa. These discrepancies may come from various difficulties in LHDAC experiments, such as those associated with kinetic problems, temperature or pressure uncertainties, effect of different starting materials, etc.

During the last two decades, a series of theoretical studies (Dubrovinsky et al., 1997; Karki et al., 1997a; Kingma et al., 1995) also addressed this issue of the post-St phase transitions in the framework of the ab initio calculations. These early theoretical studies were limited to static conditions, the calculations being performed at $T = 0 \text{ K}$, without considering the zero-point energy. To investigate the contradictory experimental results on the high-temperature phase stability of SiO_2 under high pressure, finite temperature thermal effect on the transitions obtained by these static calculations should be taken into account.

Tsuchiya et al. (2004c) predicted the high-pressure and high-temperature phase equilibrium of three ordered modifications of SiO_2 using ab initio density functional perturbation theory and the quasiharmonic approximation. The predicted St- CaCl_2 phase transition boundary is $P = 56 + 0.0059 T \text{ (K)}$ GPa, which is consistent with the results of a LHDAC experiment by Ono et al. (2002). This predicted slope of the St- CaCl_2 boundary of about 5.9 MPa K^{-1} is close to, but slightly larger than, the earlier rough estimate of 4 MPa K^{-1} (Kingma et al., 1995). The LHDAC experiment resulting in a St- α - PbO_2 boundary with a negative Clapeyron slope (Dubrovinsky et al., 2001) disagrees with the phase diagram based on Tsuchiya et al. (2004c), as shown in Figure 8. This disagreement may be due to experimental uncertainties and/or to kinetic problems in the former LHDAC experiment. These are supported by later calculations by Oganov et al. (2005a), though they proposed substantially lower transition pressures primarily due to the application of LDA (see Section 2.03.2.2).

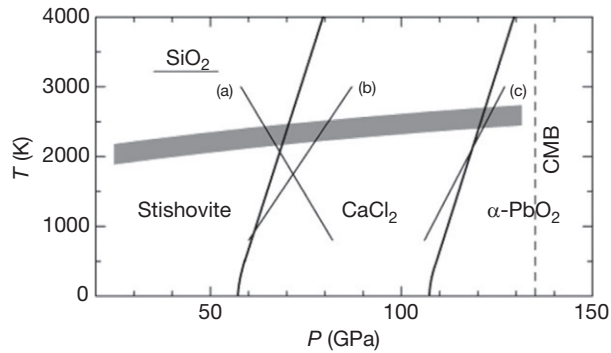


Figure 8 High P , T phase diagram for SiO_2 at lower mantle pressures predicted by the ab initio calculations by Tsuchiya et al. (2004c). The results of in situ x-ray experiments using LHDAC by (a) Dubrovinsky et al. (2001), (b) Ono et al. (2002), and (c) Murakami et al. (2003) are also shown.

On the other hand, the phase transition boundary between CaCl_2 and $\alpha\text{-PbO}_2$ in SiO_2 is predicted to be $P = 106.3 + 0.00579 T$ (K) GPa based on ab initio calculations (Tsuchiya et al., 2004c), which locates near the lowermost mantle P , T conditions. This calculation also indicates that the $\alpha\text{-PbO}_2$ -type phase is the stable form of silica at depths down to the CMB, consistent with the result of an LHDAC experiment (Murakami et al., 2003). These theoretical and experimental results also suggest that the $\alpha\text{-PbO}_2$ -type phase silica recently discovered in the meteorite sample might have been formed by a metastable reaction.

Irfune and Ringwood (1993) reported that St contains up to ~5% Al_2O_3 in a mid-ocean ridge basalt (MORB) composition under the uppermost lower mantle conditions. It was found that the aluminous St, containing Al_2O_3 of 4–6 wt%, transforms to a CaCl_2 structure at pressures of 23–25 GPa at 300 K (Bolfan-Casanova et al., 2009; Lakshtanov et al., 2007), substantially lower than those determined for pure SiO_2 St (~55–60 GPa; Ono et al., 2002; Tsuchiya et al., 2004c). Moreover, the occurrence of shear softening before the phase transition (Lakshtanov et al., 2007) and significant decreases in bulk moduli of both St and the CaCl_2 -phase (Bolfan-Casanova et al., 2009) were observed in aluminous St. The acoustic softening associated with this transition of aluminous St in subducted oceanic crust may account for the observed localized discontinuities in the lower mantle (see the succeeding text).

2.03.3.1.7 Al-rich phase

Majorite garnet is the main host of aluminum in the mantle transition region in both pyrolite and basaltic compositions. It transforms to an assemblage of $\text{Mg-Pv} + \text{Ca-Pv}$ at pressures corresponding to the uppermost lower mantle. Aluminum is incorporated mostly in Mg-Pv in pyrolite composition (Irfune, 1994), whereas a separate aluminous phase is formed in basaltic compositions under the P , T conditions of the lower mantle, as demonstrated by Irfune and Ringwood (1993).

The aluminous phase, named ‘Al-rich phase’ by these authors, was suggested to have a crystal structure similar, but not completely identical, to the calcium ferrite structure. This Al-rich phase was later proposed to have a hexagonal structure

or NAL-phase (new aluminous phase; Akaogi et al., 1999; Miyajima et al., 2001; Sanehira et al., 2005), whereas others proposed that this phase possesses the calcium ferrite structure (Hirose et al., 1999; Kesson et al., 1998; Ono et al., 2005d). More recently, it was shown that both NAL-phase and the calcium ferrite phase coexist in MORB at pressures lower than ~45–50 GPa, while the former phase disappears at higher pressures (Ricolleau et al., 2008, 2010), consistent with the phase relations in the $\text{MgAl}_2\text{O}_4\text{--NaAlSi}_3\text{O}_8$ system (see the succeeding text). In any case, only very minor effects on the mineralogy and dynamics in the lower mantle are expected upon the change between these two phases under the lower mantle conditions (Sanehira et al., 2005; Shinmei et al., 2005), as the crystal structures of these phases are quite similar and yield only a slight difference in densities.

2.03.3.2 Other Minor Minerals

2.03.3.2.1 MgAl_2O_4 , $\text{NaAlSi}_3\text{O}_8$

MgAl_2O_4 spinel is known to decompose to simple oxides of MgO and Al_2O_3 at pressure and temperatures of the mantle transition region and recombine to form a calcium ferrite (CaFe_2O_4 , CF) type phase at about 25 GPa (Akaogi et al., 1999; Funamori et al., 1998; Irfune et al., 1991). Although the formation of an unknown phase named ϵ -phase (Liu, 1978) was reported at a similar pressure at 1300 K in LHDAC experiments, none of the subsequent LHDAC and KMA experiments using both quench and in situ x-ray measurements have confirmed this phase. Instead, it has been shown that the CF-phase further transforms to a calcium titanate (CaTiO_4 , CT) phase at pressures of ~40–45 GPa (Funamori et al., 1998). An ab initio periodic linear combination of atomic orbitals calculation by Catti (2001) demonstrated that the calcium titanate structure is stable relative to the calcium ferrite structure at pressures greater than ~39–57 GPa, but this phase change was not confirmed by a recent pseudo-potential study (Tsuchiya, 2011).

$\text{NaAlSi}_3\text{O}_8$ also adopts the calcium ferrite structure at pressures above 25 GPa (Akaogi et al., 1999; Liu, 1977), although the formation of the complete solid solutions between this and MgAl_2O_4 was not reported, as there is a region of the hexagonal phase (NAL-phase) in the intermediate region of these end-member compositions (Akaogi et al., 1999; Ono et al., 2009; Shinmei et al., 2005). It was demonstrated that the CF-type $\text{NaAlSi}_3\text{O}_8$ is stable at least at pressures up to 75 GPa and temperatures to 2500 K on the basis of LHDAC experiments (Tutti et al., 2000).

More recently, the stability relations of the CF phase and the hexagonal phase in the joint $\text{NaAlSi}_3\text{O}_8\text{--MgAl}_2\text{O}_4$ were investigated both experimentally and theoretically (Imada et al., 2011; Kawai and Tsuchiya, 2012). The study demonstrated that the hexagonal phase is no more stable at pressures higher than ~45 GPa and completely transforms to the CF phase. Kawai and Tsuchiya (2012) also showed that the NAL–CF transition would not cause any notable velocity changes in the lower mantle.

2.03.3.2.2 KAlSi_3O_8 , $\text{NaAlSi}_3\text{O}_8$

KAlSi_3O_8 -rich feldspar, an important mineral in K-rich basalt (e.g., Wang and Takahashi, 1999) and continental crust

and marine sediment lithologies (Irifune et al., 1994), transforms to the hollandite structure via a mixture of $K_2Si_2O_5$ wadite + Al_2O_5 kyanite + SiO_2 coesite at about 9 GPa. $KAlSi_3O_8$ hollandite plays an important role in fractionation of some trace elements because of its peculiar tunnel structure that accommodates large ion lithophile elements (Irifune et al., 1994; Rapp et al., 2008). Although a LHDAC study suggested that this structure is stable almost throughout the lower mantle P , T conditions (Tutti et al., 2001), recent in situ x-ray diffraction studies using DAC with a helium pressure medium at room temperature (Ferroir et al., 2006) and KMA at high pressure and high temperature demonstrated that the hollandite transforms to an unquenchable phase, named 'hollandite II' (Sueda et al., 2004), at about 22 GPa at room temperature with a positive Clapeyron slope. Although only a slight modification in crystal structures between these phases was noted (Ferroir et al., 2006), this transition may significantly affect partitioning of some trace elements between the K-hollandite and coexisting melts in the lower mantle.

Ab initio calculations (Caracas and Boffa Ballaran, 2010; Kawai and Tsuchiya, 2013; Mookherjee and Steinle-Neumann, 2009) demonstrated that the transition of K-hollandite to the hollandite II structure is associated with an elastic instability as suggested by Hirao et al. (2008). Kawai and Tsuchiya (2013) further indicated clearly that the transition has the second-order nature. These studies also showed that the hollandite-II phase remains stable up to the CMB condition.

$NaAlSi_3O_8$ -rich hollandite was found in shock veins of some meteorites (e.g., Gillet et al., 2000; Tomioka et al., 2000). However, attempts to reproduce the hollandite with such compositions by high-pressure experiments have failed (Liu, 2006; Yagi et al., 1994), as the solubility of this component is limited to about 50 mol% at pressures of ~ 22 GPa and at temperatures up to 2500 K. Thus, this phase could have been formed metastably in a very short period of time under shock compression in the parental bodies of these meteorites. A recent ab initio computation supports this idea, showing that $NaAlSi_3O_8$ -rich hollandite is unstable relative to other possible phase assemblages at pressures at least to 40 GPa (Deng et al., 2010).

2.03.3.2.3 CAS phase

The 'CAS (Ca- and Al-rich silicate) phase' was first described by Irifune et al. (1994) as a new Ca- and Al-rich high-pressure phase in a continental crust composition at pressures above ~ 15 GPa and was suggested to be a major host for aluminum and calcium in the subducted marine sediments in the mantle transition region. Subsequent experimental studies demonstrated that this phase has the ideal composition of $CaAl_4Si_2O_{11}$, possessing a hexagonal barium ferrite-type structure with space group $P6_3/mmc$ (Gautron et al., 1999). Moreover, this high-pressure phase with a composition of $(Ca_xNa_{1-x})Al_{3+x}Si_{3-x}O_{11}$ was recently discovered in a Shergottite shocked Martian meteorite in association with St and/or K,Na-rich hollandite (Beck et al., 2004), both of which are known to be stable only at pressures above ~ 9 GPa.

The CAS phase is suggested to have silicon in fivefold coordination in a trigonal bipyramid site at high pressure and high temperature and is supposed to decompose into fourfold and sixfold coordinations upon quenching and subsequent

release of pressure (Gautron et al., 1999). In situ Raman spectroscopy and x-ray diffraction measurements actually indicated the formation of fivefold coordinated silicon under pressure, which should play an important role in the transport properties of minerals through the formation of oxygen vacancies (Gautron et al., 2005).

Stability of the CAS phase was determined based on high-pressure experiments at pressures to 23 GPa and temperatures to 2073 K, combined with thermodynamic analyses, showing that this phase is stable above ~ 12 GPa and at temperatures exceeding 1373 K (Akaogi et al., 2009). The low-pressure phase assemblage is reported as garnet + kyanite + corundum, while an assemblage of garnet + St + corundum is stable at the lower temperatures. It has also been reported that grossular garnet decomposes to Ca-Pv + the CAS phase at pressures above 20 GPa and temperatures higher than ~ 1400 K (Greaux et al., 2011).

2.03.3.2.4 Phase D, δ -AlOOH

Phase D was first noted by Liu (1986) as a new dense hydrous magnesium silicate (DHMS) phase in serpentine and was later confirmed by in situ x-ray diffraction (Irifune et al., 1996b). Both the x-ray power diffraction profile and the chemical composition of this phase were also refined on the quenched sample (Irifune et al., 1996b; Kuroda and Irifune, 1998). Two groups subsequently succeeded in refining its crystal structure independently (Kudoh et al., 1997; Yang et al., 1997). The stability of phase D has since been studied experimentally using both KMA (Frost and Fei, 1998; Irifune et al., 1998b; Ohtani et al., 1997) and LHDAC (Shieh et al., 1998). This demonstrated that this phase has a wide stability field up to 4050 GPa at temperatures to ~ 1800 K, whereas it dehydrates to form an assembly containing Mg-Pv and Mw at higher temperatures (Shieh et al., 1998).

Serpentine is the major hydrous mineral in the subducted slab, and phase D should be the only possible DHMS present in the upper part of the lower mantle transported via the subduction of slabs (Irifune et al., 1998b; Ohtani et al., 2004; Shieh et al., 1998), although the newly found δ -AlOOH (Suzuki et al., 2000) could be an alternative water reservoir in the lower mantle if a certain amount of water is retained in the crustal components in the subducted slabs. δ -AlOOH was both experimentally and theoretically (Sano et al., 2008; Tsuchiya and Tsuchiya, 2011a) reported to be stable under almost the entire P , T conditions of the lower mantle. The extraordinarily high stability of δ -AlOOH as a hydrous phase suggests that this phase could be a potentially important water carrier into the core. δ -AlOOH is predicted to eventually transform to a pyrite-type structure at ~ 150 GPa before its dehydration (Tsuchiya and Tsuchiya, 2011a). δ -AlOOH is also important in the context of the hydration of St because of the similarity in their crystal structures (Panero and Stixrude, 2004). Incorporation of the AlOOH component into St might significantly affect the post-St transition pressure (Lakshtanov et al., 2007).

For both phase D and δ -AlOOH, structural changes associated with hydrogen bond symmetrization are expected to occur on the basis of ab initio calculations (Tsuchiya et al., 2002, 2005a), which should affect the compressional behavior and, hence, density changes of these hydrous phases in the lower mantle. Tsuchiya (2013) recently predicted that phase

D transforms to an assemblage of St plus a new hydrous phase MgSiO_4H_2 with monoclinic symmetry in a limited pressure range between 40 and 52 GPa, based on ab initio calculations. This phase may form solid solutions with AlOOH , and should be further explored to identify the plausible hydrous phases in the lower mantle.

2.03.3.2.5 MgCO_3 , CaCO_3

Carbonates are important constituents of pelagic sediments, parts of which are supposed to subduct into the mantle. It has been shown that MgCO_3 magnesite is the major carbonate in the mantle (e.g., Biellmann et al., 1993), and its stability under high pressure has been studied using LHDAC. Magnesite was reported to be stable at pressures up to 80 GPa almost throughout the lower mantle (Fiquet et al., 2002; Gillet, 1993), but a recent in situ x-ray diffraction study demonstrated it transforms to an unknown phase (magnesite II) at pressures above ~ 115 GPa, at 2000–3000 K (Isshiki et al., 2004). Although the dissociation of magnesite into assemblages of $\text{MgO} + \text{CO}_2$ (Fiquet et al., 2002) or $\text{MgO} + \text{C} + \text{O}_2$ (Liu, 1999) was suggested on the basis of thermodynamic considerations, such reactions are unlikely to occur along appropriate geotherms in the lower mantle (Isshiki et al., 2004; Oganov et al., 2008). Oganov et al. (2008) also predicted the formation of other high-pressure forms of MgCO_3 in the lowermost part of the mantle, which are different from the magnesite II reported by Isshiki et al. (2004). Accordingly, the stable structure of MgCO_3 in this region of the mantle remains an open question.

In contrast, certain amounts of CaCO_3 could survive in the subducted slabs without decarbonation or reaction with surrounding minerals, due to the low temperatures of the slabs, and thus are delivered into the lower mantle. CaCO_3 adopts the aragonite structure under P , T conditions of the uppermost mantle, and this was found to transform to a high pressure form with an orthorhombic symmetry at pressures greater than ~ 40 GPa and at temperatures 1500–2500 K using LHDAC (post-aragonite phase; Ono et al., 2005c). Although the possibility of the transformation of CaCO_3 aragonite to a trigonal phase is suggested on the basis of DAC experiments at room temperature (Santillán and Williams, 2004), this phase was demonstrated to have been metastably formed and the transformation of the post-aragonite phase into an orthopyroxene-type structure (post-postaragonite phase) was

confirmed at pressures above ~ 130 GPa and temperatures above ~ 1500 K by in situ x-ray observations (Ono et al., 2007), as predicted by an ab initio study (Oganov et al., 2006). Thus, MgCO_3 and possibly CaCO_3 are the potential hosts of CO_2 throughout most parts of the lower mantle, except for the bottom parts of the D'' layer (Isshiki et al., 2004; Oganov et al., 2008).

2.03.4 Phase Transitions and Density Changes in Mantle and Slab Materials

2.03.4.1 Chemical Compositions and Density Calculations

Subducting oceanic lithosphere is modeled by layers of basaltic oceanic crust of ~ 6 km thickness, underlain by thicker layers (~ 50 – 100 km) of residual harzburgite and fertile lherzolite, which are covered with thin (~ 1 km) terrigenous and/or pelagic sediments. Typical chemical compositions of these lithologies are listed in Table 1. Most parts of the sedimentary materials are believed to be trapped to form accretion terrains underneath island arcs upon subduction of slabs at ocean trenches, although geochemical evidence suggests certain parts of such materials may be subducted deeper into the mantle (e.g., Loubet et al., 1988). At least part of the bottom warmer lherzolite layer of a slab may also be assimilated to the surrounding mantle during subduction in the upper mantle and mantle transition region, and thus the slab approaching the 660 km seismic discontinuity can reasonably be modeled by a layered structure of basaltic and harzburgitic rocks (Ringwood and Irifune, 1988).

The chemical composition of the lower mantle has been a major controversial issue in the mineralogy of the Earth's interior. Some (e.g., Ringwood, 1962) believe peridotitic or pyrolitic materials are dominant in the whole mantle, while others (e.g., Anderson, 1989; Hart and Zindler, 1986; Liu, 1982) claim more Si-rich chondritic materials should be representative for the composition of the lower mantle (Table 1). The difference is based on rather philosophical arguments on the origin and subsequent differentiation processes of the Earth, which are critically dependent on the models of condensation/evaporation processes of elements and compounds in the primordial solar system and the possible formation of a deep magma ocean in the early stage of the formation of the Earth. As the elastic properties, particularly those related to

Table 1 Representative chemical compositions of lower mantle and those related to subducting slabs

	<i>Lower mantle</i>				
	<i>Chondrite</i>	<i>Pyrolite</i>	<i>Harzburgite</i>	<i>MORB</i>	<i>Continental crust</i>
SiO_2	53.8	44.5	43.6	50.4	66.0
TiO_2	0.2	0.2	–	0.6	0.5
Al_2O_3	3.8	4.3	0.7	16.1	15.2
Cr_2O_3	0.4	0.4	0.5	–	–
FeO	3.5	8.6	7.8	7.7	4.5
MgO	35.1	38.0	46.4	10.5	2.2
CaO	2.8	3.5	0.5	13.1	4.2
Na_2O	0.3	0.4	–	1.9	3.9
K_2O	–	0.1	–	0.1	3.4

Chondrite, Liu (1982); pyrolite, Sun (1982); harzburgite, Michael and Bonatti (1985); MORB, Green et al. (1979); continental crust, Taylor and McLennan (1985).

shear moduli, of high-pressure phases have not been well documented under the pressure and temperature conditions of the lower mantle, it is hard to unambiguously evaluate the feasibility of these two alternative composition models in the light of mineral physics and seismological observations (e.g., Bina, 2003; Mattern et al., 2005). Some efforts have been made to directly measure the elastic properties under the P , T conditions of the lower mantle (Murakami et al., 2012), but we need further data on the elastic properties of major minerals in the lower mantle and their pressure, temperature, and compositional dependencies to reach a decisive conclusion on the feasible chemical composition. Moreover, the knowledge of variation of temperature with depth is vital to address this issue, but this also has not been well constrained in the lower mantle.

Here, we assume the whole mantle is of a pyrolytic composition to address the phase transitions and associated density changes in the lower mantle, as there are significant chemical variations in the chondritic models and also because high-pressure experimental data on these compositions have been scarce to date. We also assume the major lithologies transported into the lower mantle via subduction of slabs are of MORB and harzburgite compositions. Some recent studies suggest that the continental crust may also be delivered to the mantle transition region (Ichikawa et al., 2013; Kawai et al., 2013), but it should be difficult to subduct further into the lower mantle, considering the density relations between the continental crust material and surrounding mantle at around the 660 km discontinuity (Irfune et al., 1994; Ishii et al., 2012; Kawai et al., 2013). Phase transitions in MORB have been extensively studied down to the depths near the mantle–core boundary. In contrast, although virtually no experimental data exist on harzburgite compositions in this depth region, they can be reasonably estimated from those available on the high-pressure phases with simple chemical compositions, as harzburgitic compositions have a minor amount of Fe and only very small amounts of Ca, and Al, and are well approximated by the MgO (FeO)–SiO₂ system.

We calculated the density changes in pyrolyte, harzburgite, and MORB compositions using available experimental data as follows: The densities of the individual high-pressure phases appeared in these lithologies were calculated at given pressures using the thermal EoS combining third-order Birch–

Murnaghan EoS and Debye theory along an appropriate geotherm, using the PVT-EoS parameters given in Table 2. The resultant density changes of individual phases along the geotherm are depicted in Figure 9. The density changes in the bulk rocks were then calculated using the proportions of the individual phases with pressure along the geotherm.

Although some recent studies suggest that sub-adiabatic temperature gradients are required to match the observed and calculated density and bulk sound velocity for pyrolytic compositions (Bina, 2003; Mattern et al., 2005), we simply assumed adiabatic temperature changes throughout the lower mantle (i.e., 1900 K at 660 km and 2450 K at 2890 km with an averaged gradient of $dT/dz \sim 0.3 \text{ K km}^{-1}$; e.g., Brown and Shankland, 1981) as such conclusions are not robust, given the uncertainties in both mineral physics measurements and seismological observations. In addition, significantly sharp temperature increases are expected to occur near the mantle–core boundary and presumably near the 660 km discontinuity as these regions are accompanied by chemical changes and form thermal boundary layers, which are also not taken into account in the present calculations.

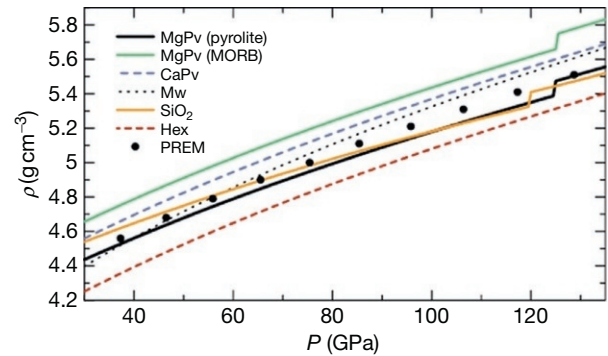


Figure 9 Density changes in major minerals constituting pyrolyte and mid-ocean ridge basalt (MORB) compositions as a function of pressure along the adiabatic geotherm, calculated with EoS using the mineral physics parameters listed in Table 2. The density changes of Mg-Pv and Mw in the harzburgite composition are very close to, but slightly lower than, those of the corresponding phases in pyrolyte, which are not shown in this figure. Dots represent the densities in PREM. Hex, hexagonal aluminous phase.

Table 2 PVT-EoS parameters of lower mantle phases determined from various experimental and theoretical data and their systematics

	Mg-Pv	Fe-Pv	Al ₂ O ₃ -Pv	Mg-PPv	Ca-Pv	MgO	FeO	SiO ₂ -St	SiO ₂ -α-PbO ₂
V_0 (cm ³ mol ⁻¹)	24.45	25.48	24.77	24.6	27.45	11.36	12.06	14.02	13.81
B_0 (GPa)	257	281	232	226	236	158	152	314	325
B'	4.02	4.02	4.3	4.41	3.9	4.4	4.9	4.4	4.2
Θ_D (K)	1054	854	1020	1040	984	725	455	1044	1044
γ	1.48	1.48	1.48	1.55	1.53	1.5	1.28	1.34	1.34
q	1.2	1.2	1.2	1.2	1.6	1.5	1.5	2.4	2.4

Mg-Pv (Fiquet et al., 2000; Shim and Duffy, 2000; Sinogeikin et al., 2004; Tsuchiya et al., 2004a, 2005b), Fe-Pv (Jeanloz and Thompson, 1983; Kiefer et al., 2002; Mao et al., 1991; Parise et al., 1990), Al₂O₃-Pv (Thomson et al., 1996; Tsuchiya et al., 2005c), Mg-PPv (Tsuchiya et al., 2004a, 2005b), Ca-Pv (Karki and Crain, 1998; Shim et al., 2000b; Wang et al., 1996), MgO (Fiquet et al., 1999; Sinogeikin and Bass, 2000), FeO (Jackson et al., 1990; Jacobsen et al., 2002; Systematics), SiO₂ (Andrault et al., 2003; Karki et al., 1997a; Ross et al., 1990; Tsuchiya et al., 2004c).

The high- T Birch–Murnaghan equation was applied only for the hexagonal aluminous phase with parameters: $V_0 = 110.07 \text{ cm}^3 \text{ mol}^{-1}$, $B_0 = 185.5 \text{ GPa}$, $B' = 4$ (fix), $dB/dT = -0.016 \text{ GPa K}^{-1}$, and $\alpha_0 = 3.44 \times 10^{-5} \text{ K}^{-1}$ (Shinmei et al., 2005; Sanehira et al., 2005).

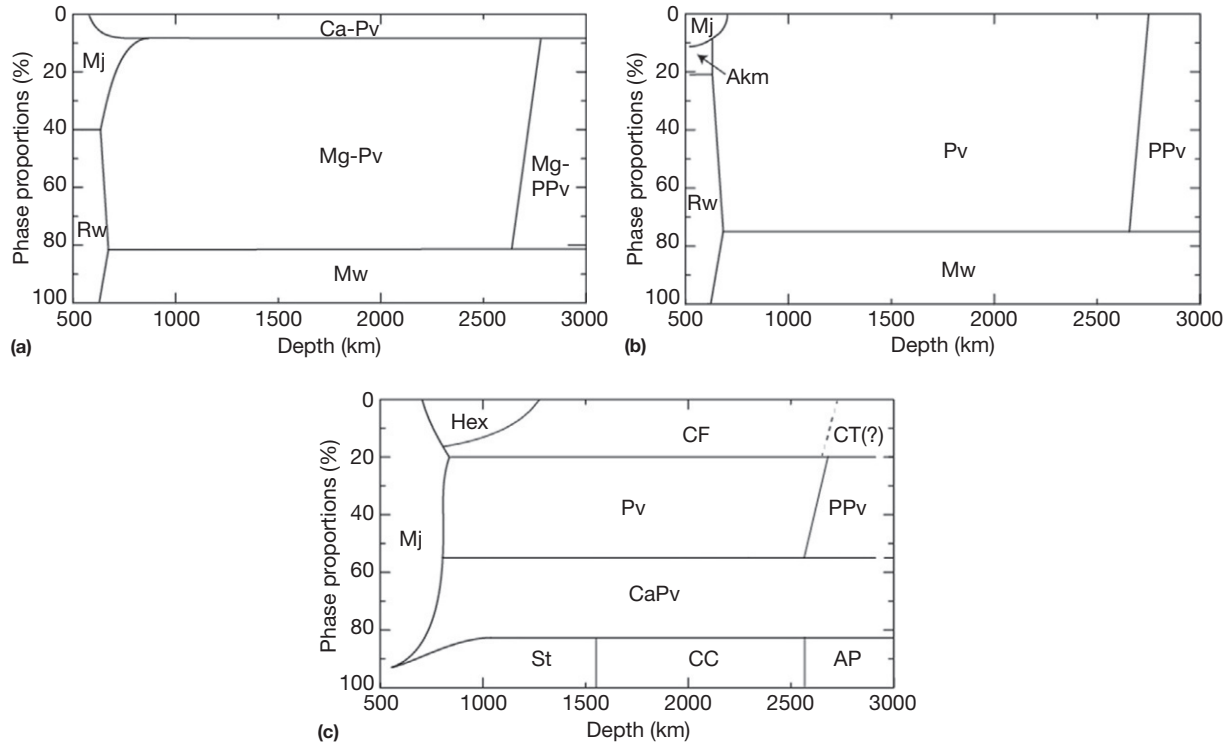


Figure 10 Mineral proportion changes in pyrolite (a), harzburgite (b), and MORB (c) as a function of depth along the adiabatic geotherm. Akm, akimotoite; Rw, ringwoodite; CF, calcium-ferrite phase; CT, calcium-titanite phase; CC, CaCl_2 phase; AP, $\alpha\text{-PbO}_2$ phase. Data taken from Irifune and Ringwood (1987, 1993), Irifune (1994), Hirose et al. (1999, 2005), Murakami et al. (2004a, 2005), Ono et al. (2001, 2005d), Irifune et al. (2010), and Ricolleau et al. (2010).

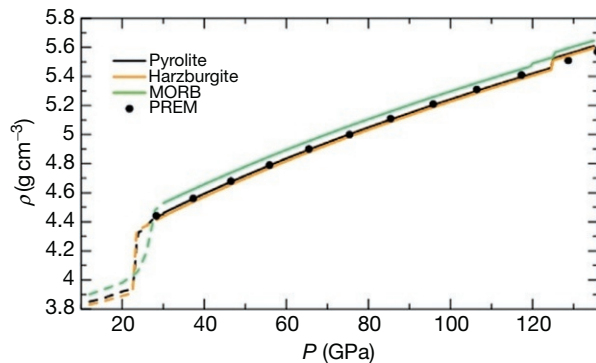


Figure 11 Bulk density variations of pyrolite, harzburgite, and MORB calculated based on the PVT-EoS of constituent mineral phases (Table 1 and Figure 9) and their proportions (Figure 10). Broken lines at pressures lower than 30 GPa are results in Irifune (1993).

The mineral proportion changes in pyrolite, harzburgite, and MORB compositions are shown in Figure 10, while the calculated density changes of these lithologies are depicted in Figure 11. The density changes at pressures lower than 30 GPa are based on an earlier estimate of Irifune (1993), using a similar method and mineral physics parameters. Although the density change in pyrolite seems to agree well with that of PREM (Preliminary Reference Earth Model; Dziewonski and Anderson, 1981), the latter estimate inevitably has significant uncertainties, as this density profile is rather indirectly

determined from seismic velocities with some assumptions. The calculated density values may also have significant errors, mainly due to the uncertainty in the geotherm stated in the above. Nevertheless, mineral physics parameters to constrain the density have been reasonably well determined, mostly on the basis of in situ x-ray diffraction measurements, and the differences among these calculated density profiles are regarded as robust results.

2.03.4.2 Phase and Density Relations

2.03.4.2.1 Pyrolite

Figure 10(a) illustrates the phase transitions in pyrolite as a function of depth. Pyrolite transforms from an assemblage of ringwoodite (Rw) + majorite garnet (Mj) + Ca-Pv under the P , T conditions of the mantle transition region to that of Mg-Pv + Ca-Pv + Mj + Mw at depths near the 660 km seismic discontinuity. The spinel to postspinel transition in this composition is actually believed to have occurred at pressures near 23.5 GPa and at a temperature of ~ 2000 K, on the basis of quench experiments (e.g., Irifune, 1994). The slope of this phase transition boundary has also been determined by both quench experiments (Ito and Takahashi, 1989) and calorimetric measurements (Akaogi and Ito, 1993), yielding a value of ~ -3 MPa K^{-1} . Although some recent studies suggest somewhat lower transition pressures (Fei et al., 2004; Irifune et al., 1998a,b; Katsura et al., 2003; Kono et al., 2010; Tange et al., 2009a) and larger Clapeyron slope (Fei et al., 2004; Katsura

et al., 2003), the spinel to postspinel transition is generally believed to be the main cause of the 660 km discontinuity, which is followed by the smeared out transition of majorite to Pv over a pressure interval of ~ 2 GPa (Irifune, 1994; Nishiyama et al., 2004).

Mg-Pv is stable throughout most regions of the lower mantle, but it is found to transform to the Mg-PPv with the CaIrO_3 structure in a peridotite composition at pressures close to those near the top of the D'' layer. A small density jump of about 1–1.5% is expected to occur associated with this transition in the lower mantle. Ca-Pv, on the other hand, is likely to adopt the cubic structure throughout the lower mantle. On the other hand, Mw remains in the rock salt (B1) structure at pressures to ~ 80 GPa, where it may transform to the NiAs (B8) structure if iron concentration is very high (Fei and Mao, 1994). A high-spin to low-spin transition has also been demonstrated to occur in this phase over the pressure range of the upper to middle lower mantle, as shown in Figure 6, which may yield an additional gradual density increase over this interval and also affect partitioning of iron between this phase and the ferro-silicate Pv (Irifune et al., 2010).

Although element partition data among the coexisting phases under the lower mantle conditions have been limited to those below ~ 50 GPa in KMA for the pyrolite composition (e.g., Irifune, 1994; Irifune et al., 2010; Wood, 2000), some results have also been obtained using LHDAC combined with ATEM at higher pressures (e.g., Murakami et al., 2005; Ono et al., 2005d; Sinmyo and Hirose, 2013). These studies, particularly those using KMA, demonstrated that the presence of a minor amount (~ 5 wt%) of Al_2O_3 in Mg-Pv has dramatic effects on the partitioning of iron between Mg-Pv and Mw, in addition to those on the compressibility of Mg-Pv, below ~ 30 GPa. Nevertheless, the variations in iron partitioning between the two phases would not cause any significant changes in the bulk density of the pyrolitic mantle (e.g., Bina, 2003; Irifune et al., 2010). Some notable changes in the iron partitioning between Mg-Pv and Mw have also been suggested upon the Pv-PPv transition in a recent LHDAC study (Murakami et al., 2005; Sinmyo et al., 2011), but it may also yield invisible effects on the density change in the pyrolite bulk composition.

2.03.4.2.2 Harzburgite

Harzburgite, with $\text{Mg\#} (= \text{Mg}/(\text{Mg} + \text{Fe}) \times 100) = \sim 92$ as listed in Table 1, crystallizes to form an assemblage of $\sim 80\%$ olivine and $\sim 20\%$ orthopyroxene at depths in the uppermost mantle, which transforms to Mg-Pv and Mw near the 660 km discontinuity via an assemblage of $\text{Rw} + \text{Mj} + \text{akimotoite}$ (Akm, ilmenite form of MgSiO_3) as shown by Irifune and Ringwood (1987). Although no experimental data have been available at pressures higher than 26 GPa, the nature of the phase transition in this composition can be evaluated based on the changes in these two phases under the lower mantle conditions. The result estimated along the adiabatic geotherm is shown in Figure 10(b), which shows that this lithology is less dense than pyrolite throughout the lower mantle except for a very limited region immediately below the 660 km discontinuity (Irifune and Ringwood, 1987), where the density relation reverses due to the completion of the spinel to postspinel transition at lower pressures in the harzburgite composition.

It was suggested that Fe significantly lowers the Pv-PPv transition pressure (Mao et al., 2004, 2005), while more recent studies showed that the effect of iron on this transition pressure is rather opposite (Andrault et al., 2010; Hirose et al., 2008; Sinmyo et al., 2008) as stated earlier. On the other hand, the presence of Al may also slightly affect this transition pressure (Tateno et al., 2005; Tsuchiya and Tsuchiya, 2008; Tsuchiya et al., 2005c), as shown in Figures 2–4. In harzburgite compositions, Mg-Pv should have less alumina and iron content as compared with those of Mg-Pv in pyrolite under the lower mantle conditions. However, as the differences in the contents of Fe and Al between these two lithologies are relatively small, we assume the Pv-PPv transition occurs at the same pressure in these compositions, although further detailed experimental studies on these compositions are needed to resolve this issue.

2.03.4.2.3 Mid-ocean ridge basalt

Phase transitions in basaltic compositions, such as illustrated in Figure 10(c) for a MORB composition, are quite different from those expected in pyrolite and harzburgite compositions. Basaltic compositions are shown to crystallize to $\text{Mj} + \text{small amounts of St}$ in the mantle transition region (Hirose et al., 1999; Irifune and Ringwood, 1987, 1993; Ono et al., 2001), and then progressively transform to an assemblage of $\text{Ca-Pv} + \text{Mg-Pv} + \text{St} + \text{Al-rich phase}$ (NAL phase, which is replaced by the CF phase at pressures greater than ~ 50 GPa according to Ricolleau et al., 2010) over a wide pressure range of ~ 3 GPa (from ~ 24 to ~ 27 GPa). Although the garnetite facies of MORB, composed mainly of Mj , are substantially denser than pyrolite, a density crossover is expected to occur in a limited depth range (660 to ~ 720 km) of the uppermost lower mantle due to this smeared-out nature of the garnetite to Pv transition in MORB.

Once Ca-Pv and Mg-Pv are formed in basaltic compositions, it is shown that they become denser than pyrolite or peridotite throughout almost the entire region of the lower mantle (Hirose et al., 1999, 2005; Irifune and Ringwood, 1993; Ono et al., 2001, 2005d). As St is highly incompressible (Figure 9), the density of the perovskite facies of basaltic compositions may approach that of the pyrolitic composition with increasing pressure. However, the transition of St to CaCl_2 (CC) and $\alpha\text{-PbO}_2$ (AP) structures should keep this lithology denser than pyrolite throughout the lower mantle, as shown in Figure 11. In fact, most recent experimental studies using LHDAC (Hirose et al., 2005; Ono et al., 2005d; Ricolleau et al., 2010) conclude that densities of basaltic compositions are higher than those in the representative model mantle compositions throughout the lower mantle by about $0.02\text{--}0.08 \text{ g cm}^{-3}$, depending on the adopted pressure scale for gold.

2.03.5 Mineralogy of the Lower Mantle

2.03.5.1 The 660 km Discontinuity

The 660 km seismic discontinuity is a globally recognized feature, and is the sharpest among the proposed discontinuities throughout the whole mantle. The cause of this discontinuity (chemical or phase transition boundary) has been a major controversial issue in Earth sciences as stated

earlier, but the detailed experimental study based on quench experiments using KMA strongly suggested that this is caused by the spinel to postspinel transition in a pyrolite or peridotitic mantle (Irifune, 1994; Ito and Takahashi, 1989). The experimental data on the sharpness, pressure, and Clapeyron slope of this phase transition all seemed to be consistent with those estimated from seismological observations.

However, recent experimental, seismological, and geodynamic studies cast some doubt on the simple idea of the phase transition. Precise in situ x-ray diffraction measurements using KMA demonstrated that this transition occur at pressures somewhat (~ 2.5 – 1 GPa) lower than that corresponding to the 660 km discontinuity (Fei et al., 2004; Irifune et al., 1998a; Katsura et al., 2003; Matsui and Nishiyama, 2002; Nishiyama et al., 2004), although some LHDAC experiments reported the phase transition pressure is rather consistent with that of the discontinuity (Chudinovskikh and Boehler, 2001; Shim et al., 2001a). Meanwhile, reevaluation of the transition pressure using the latest MgO pressure scales based on a theoretical analysis (Tange et al., 2009a) and sound velocity measurement (Kono et al., 2010) shows that the pressure for the spinel to postspinel transition is close to, but slightly (~ 0.5 – 1 GPa) lower than, that of the 660 km discontinuity. In addition, seismological observations suggest this discontinuity is divided into several discontinuities in some areas (e.g., Simmons and Gurrola, 2000), which cannot be explained by the spinel to postspinel transition alone.

Moreover, recent in situ x-ray diffraction measurements have suggested that the Clapeyron slope of the spinel to postspinel transition is significantly larger (-2 to -0.4 MPa K $^{-1}$; Fei et al., 2004; Katsura et al., 2003; Litasov et al., 2005) than previously thought (~ -3 MPa K $^{-1}$; Akaogi and Ito, 1993; Ito and Takahashi, 1989) and ab initio prediction (~ -2 MPa K $^{-1}$; Yu et al., 2006). If this is the case, it should be difficult to trap the subducted slabs underneath many subduction zones near this boundary, known as ‘stagnant slabs’ (e.g., Fukao et al., 1992, 2001; Zhao, 2004), in the light of geodynamics calculations (e.g., Davis, 1998), unless a large viscosity jump at the 660 km depth and a concept of trench retreat are introduced (Torii and Yoshioka, 2007). Furthermore, the observed depth variations of the 660 km discontinuity sometimes reach ~ 30 – 40 km (e.g., Flanagan and Shearer, 1998), which corresponds to a temperature difference of ~ 1000 K if we adopt $dP/dT = -1$ MPa K $^{-1}$ for the spinel–postspinel transition boundary. Such a temperature difference between subducting slabs and the surrounding mantle near the 660 km discontinuity should be too large to be accounted for by seismological tomographic observations or by any reasonable models of thermal structures of the subducting slabs.

Nevertheless, considering the uncertainties in pressure and temperature measurements in the in situ x-ray observations in KMA due to unresolved problems on the pressure scales and temperature measurements at high pressure using thermocouple electromotive force, it is generally accepted that the 660 km discontinuity can be explained by the spinel–postspinel transition in a pyrolitic mantle. Recent studies also suggested possibilities of elucidating the multiple nature and the depth variation of the 660 km discontinuity by reactions involving akimotoite at relatively low temperatures (Hirose, 2002; Weidner and Wang, 2000; Zhou et al., 2013). In this case, the

high velocity/density gradients shown in some representative seismological models at depths of 660–750 km may be largely explained by the smeared-out transition of majorite to perovskite in pyrolite over this depth interval (Irifune, 1994).

Models with chemical composition changes may reconcile the contradictory experimental and seismological observations regarding the 660 km discontinuity. If the spinel to postspinel transition does occur at pressures lower than that of 660 km (~ 23.5 GPa) by, for instance, 1 GPa, the phase discontinuity should locate at about 630 km in a pyrolite mantle. As the oceanic crust component of the subducted slab, modeled by the MORB composition, becomes less dense than the surrounding pyrolite mantle immediately below this depth as shown in Figure 11, it should have been buoyantly trapped on this primordial ‘630 km discontinuity’ at the initial stage of the onset of operation of plate tectonics.

The delamination and accumulation of the former oceanic crust, transformed to garnetite in the mantle transition region, can be enhanced by its plausible different viscosity relative to the surrounding mantle (Karato, 1997) and extremely slow reaction kinetics upon transitions to the denser phase assemblages including Mg-Pv (Kubo et al., 2002) or majorite (Nishi et al., 2011). Continuation of this process of trapping basaltic crust over a couple of billion years should yield a thick (on average ~ 50 – 100 km, depending on the production rates of oceanic crust and efficiency of the trapping) layer of garnetite near the 630 km discontinuity. The garnetite layer develops both upward and downward from this primordial discontinuity if it isostatically floats on this boundary. The bottom of this garnetite layer eventually reaches 660 km, under which the harzburgite portion of the subducted slab should be present. In fact, some mineral physics studies suggest the uppermost lower mantle can be Mg-rich as compared with the deeper regions (Bina, 2003; Nakagawa et al., 2010).

Accumulation of oceanic crust above the 660 km seismic discontinuity was originally proposed by Anderson (1979) to form an eclogite layer in the lower half of the upper mantle and throughout the mantle transition region. He later confined it to the latter region and favored a more mafic lithology named ‘piclogite’ (e.g., Anderson and Bass, 1986; Duffy and Anderson, 1989). Ringwood (1994) also proposed the presence of a thin ($\sim <50$ km) layer of former basaltic crust immediately above the lower mantle, as a result of accumulation of relatively young and warm slab materials at the 660 km discontinuity. The above model of a thicker garnetite layer is thus in between those proposed by these authors. Some numerical analyses with seismological data (Camarano et al., 2009) and geodynamic modeling (Nakagawa et al., 2010) using available mineral physics data also suggest that the proportion of MORB would increase with depth in the mantle transition region.

On the other hand, recent developments in combined in situ x-ray and ultrasonic interferometry measurements in KMA allowed us to precisely determine sound velocities of high-pressure minerals under the pressure and temperature conditions of the mantle transition region (Higo et al., 2008; Li, 2003). The results using this technique demonstrated that both pyrolite and MORB compositions fail to explain the seismological velocity models for the lower parts of the mantle transition region (Irifune et al., 2008; Kono et al., 2012), consistent with the results of ab initio calculations (Tsuchiya,

2011). Irifune et al. (2008) suggested that the bottom parts of the mantle transition region may be filled with harzburgite instead of MORB, as discussed above, and may be the main body of the subducted slabs. Further studies are needed to identify the chemical composition of this region of the mantle around 660 km, which is important in addressing the nature and origin of this largest seismic discontinuity in the mantle.

2.03.5.2 Middle Parts of the Lower Mantle

The uppermost part of the lower mantle is believed to be structurally and chemically heterogeneous due to the presence of stagnant slabs (Fukao et al., 1992, 2001; Zhao, 2004) which were originally proposed as ‘megaliths’ on the basis of high-pressure experimental studies (Ringwood, 1994; Ringwood and Irifune, 1988). Moreover, there are some areas where slabs appear, from tomographic images, to penetrate deep into the lower mantle (e.g., Fukao et al., 2001; van der Hilst et al., 1997), which should contribute to the observed reflection, refraction, or conversion of seismic waves at these depths. Thus, the presence of subducted slabs in the uppermost lower mantle may, at least partly, contribute to the transitional nature of the seismic velocities for a depth interval between 660 and ~750 km in some global models of the velocity profiles.

In the deeper parts of the lower mantle, discontinuous changes in seismic velocities have also been suggested to occur, particularly at depths 900–1200 km beneath some subduction areas (Kaneshima, 2003; Kawakatsu and Niu, 1994; Kruger et al., 2001; Niu and Kawakatsu, 1996). As there are no major phase transitions in the mantle material modeled by pyrolite as shown in Figure 10(a), such discontinuous changes are most likely to be related to the subducted slab materials. Both basaltic and underlying harzburgite layers of such slabs may yield locally high acoustic impedance to produce seismic discontinuities, because these basaltic and harzburgite materials seem to have seismic velocities higher than those of the mantle material in this region of the lower mantle (e.g., Bina, 2003), in addition to their lower temperatures compared to the surrounding mantle.

In further deeper parts of the lower mantle (~1200–1850 km in depth), the presence of seismic scattering bodies with a low velocity signature was recognized (Kaneshima and Helffrich, 1999, 2003; Vinnik et al., 2001). As shown earlier, the most notable phase transition in major minerals in subducted slab and the surrounding mantle materials is the rutile to CaCl_2 transition of SiO_2 in subducted former oceanic crust under the P , T conditions of the middle part (~1600 km, corresponding to pressures of ~70 GPa; Tsuchiya et al., 2004c) of the lower mantle. A significant shear softening is expected to occur in St associated with this phase transition (Andrault et al., 1998; Karki et al., 1997b; Shieh et al., 2002). Thus, this transition in subducted basaltic material may explain the signatures of the scatterers observed in the middle part of the lower mantle. In contrast, the electronic spin transition in Mw in the upper to middle regions of the lower mantle may yield some variations in sound velocities, but these changes are rather gradual and probably seismologically invisible (e.g., Lin et al., 2013).

Tomographic imaging and other seismological studies demonstrate that only little anomalous changes in seismic velocities exist in the middle to lower part of the lower mantle except for regions related to subducted slabs and rising plumes (e.g., Grand et al., 1997; Mattern et al., 2005; Zhao, 2004). As shown in the previous section, no major phase changes have been reported in Mg-Pv, Ca-Pv, and Mw at pressures up to ~120 GPa, except for the slight distortion of cubic Ca-Pv to a tetragonal structure and the spin transitions in both Mg-Pv and Mw. It is expected that the transition in Ca-Pv may not occur at temperatures of the lower mantle, while the spin transitions should occur continuously over a wide pressure range as shown in Figures 7 and 6, respectively. Accordingly, both of these transitions would not cause any notable seismic velocity changes in this region, although further study is required to address the effects of the possible dissociation of Mw mentioned earlier. Thus, the relatively homogeneous nature in seismic velocity distributions in the middle to lower parts of the lower mantle is consistent with the absence of major phase transitions in the mantle material.

On the other hand, seismological, geochemical, and geodynamic studies suggest that there should be a chemically distinct regions at depths below 1500–2000 km, presumably due to iron-enrichment related to the primitive mantle materials or interaction with the rising hot plumes (e.g., Ishii and Tromp, 1999; Kellogg et al., 1999; Trampert et al., 2004). Attempts have been made to estimate the chemical composition of the lower mantle by mineral physics tests (e.g., Bina, 2003; Jackson and Rigden, 1998; Mattern et al., 2005), comparing calculated densities and bulk sound velocities of various compositions with those obtained seismologically. However, it is difficult to constrain the chemical composition of the lower mantle without reasonable estimations of thermal structures in this region and of shear properties of the relevant high-pressure phases. Actually, a wide range of chemical compositions from peridotite to chondrites can be accommodated for the acceptable geotherms, although anomalously high X_{Mg} ($=\text{Mg}/(\text{Mg}+\text{Fe})$) and low X_{Pv} ($=\text{Si}/(\text{Mg}+\text{Fe})$) and low X_{Mg} and high X_{Pv} are suggested in the uppermost and lowermost ~200 km of the lower mantle, respectively (Bina, 2003).

The possible iron and silica rich nature in the bottom part of the lower mantle may reflect the heterogeneous chemical composition and mineralogy of this region. These silicon-rich signatures can be explained by the presence of subducted oceanic crust materials in this region, which are denser than the surrounding pyrolitic or harzburgitic lower mantle materials, as shown in Figure 11, although the fraction of the basaltic component can significantly vary depending on its composition (Nakagawa et al., 2010). The CaCl_2 - α - PbO_2 transition in SiO_2 is calculated to take place at 120–125 GPa and 2000–2500 K (Tsuchiya et al., 2004c), which should stabilize the SiO_2 -bearing basaltic material in the D'' layer. Moreover, SiO_2 is also expected to exist in this region as a product of the reaction between the solid silicate Pv (or PPv) of the mantle and the molten Fe of the outer core (Knittle and Jeanloz, 1991).

In contrast, the Mg-rich and Si-poor refractory nature of the uppermost part of the lower mantle suggested by Bina (2003) could be due to the presence of accumulated harzburgite-rich bodies of the stagnant slabs (Fukao et al., 1992; Irifune et al.,

2008; Nakagawa et al., 2010; Ringwood and Irifune, 1988). This is mainly because harzburgite is less dense than pyrolite throughout the lower mantle, as is seen in Figure 11. Nevertheless, the density difference is not so large, and the thermal anomalies due to subduction of slabs or rising plumes may be more effective in circulation of the harzburgitic materials within the lower mantle.

2.03.5.3 PPv Transition and the D'' Layer

The bottom ~200 km of the lower mantle is known as a highly heterogeneous region on the basis of seismological observations, named as the D'' layer to distinguish it from the grossly homogeneous part of the lower mantle above (region D; Bullen, 1949). The horizontally and vertically heterogeneous nature of the D'' layer is primarily because this region is the chemical boundary layer between convective rocky mantle and molten iron core, which inevitably produces a large thermal boundary layer ($\Delta T > \sim 1000$ K; e.g., Williams, 1998) and accordingly yields active reactions of mantle and core materials (e.g., Knittle and Jeanloz, 1991), partial melting of mantle and slab materials (Lay et al., 2004), generation of hot mantle plumes (Garnero et al., 1998), etc. Various models have been proposed to account for the observed complex seismological signatures of D'' as reviewed by Garnero et al. (2004).

The recent finding of the Pv–PPv transition in MgSiO_3 has dramatically affected the conventional interpretations of the complex and heterogeneous features of the D'' layer. Many researchers in different research fields of Earth sciences, including mineral physics, seismology, geochemistry, mantle dynamics, etc., have started studies relevant to these topics, and a number of papers have been published immediately after the appearance of the first report on this issue (Murakami et al., 2004a). The rate of data accumulation is so fast and the relevant research fields so vast that we are unable to thoroughly evaluate all of these studies at this time. So, instead of discussing the origin of the D'' layer based on rather immature knowledge in these broad research fields, we herein summarize and examine currently available phase relations and some physical properties of the PPv in terms of high-pressure experimental and theoretical points of view. We will discuss the subject and speculate on the nature of the D'' layer within these mineral physics frameworks.

Now, what is most robust is that the Pv–PPv transition in MgSiO_3 does occur at pressures near the D'' layer on the basis of both high-pressure experiments and ab initio calculations. Also true is the fact that the latter phase adopts the crystal structure of CaIrO_3 type as evident from all of these studies. The density increase in Mg–Pv associated with this transition is most likely to be only 1.2–1.5% as constrained experimentally and predicted by ab initio calculations. The remarkable agreements among these independent studies on both experimental and theoretical bases strongly suggest that these should be regarded as facts beyond any doubts.

On the other hand, there are some uncertainties in the phase transition pressure and its temperature dependency. The pressures calculated with different scales in DAC experiments, even for those based on the EoS of gold, may differ by as much as 10–15 GPa at pressures of D'' layer (~120–136 GPa) due to the inaccuracy of the EoSs of pressure reference

materials as discussed earlier (see Figure 1), and accordingly this transition could be realized only at pressures of the outer core (Shim et al., 2004). Moreover, uncertainties in temperature measurements in LHDAC at these very high pressure regions are fairly large, and are generally ± 10 –20% of the nominal values. These yield additional uncertainties of greater than 2–5 GPa in pressure measurements in LHDAC. Thus, the errors of the transition pressure can be $\sim \pm 20$ GPa for the Pv–PPv transition in MgSiO_3 within the current state-of-the-art LHDAC technology. Moreover, it is fair to say that the Clapeyron slope of this transition has been virtually unconstrained by LHDAC experiments.

In contrast, remarkably good agreement in phase transition pressures (~110 GPa, at 0 K) and the Clapeyron slopes (7–10 MPa K^{-1}) have been obtained in some independent ab initio calculations (Oganov and Ono, 2004; Tsuchiya et al., 2004a), and these are consistent with the experimental results and also with what are expected from seismological observations (Sidorin et al., 1999). The mutual agreement among the results of the ab initio calculations, however, does not warrant the validity of these values, as these authors used basically the same technique with only some relatively minor difference in computational methods and techniques. Thus, these results on the Pv–PPv phase boundary based on ab initio calculations should be further tested on the basis of experimental studies before they are regarded as robust ones.

Nevertheless, there is no strong evidence against the occurrence of the Pv–PPv transition at pressures about 120 GPa, with a Clapeyron slope of 7–10 MPa K^{-1} , and it is reasonable to tentatively take these values as realistic ones. It has been reported that such a large Clapeyron slope is expected to affect the thermal structure of the lower mantle and, thus, enhances the mantle convection and plume dynamics (Nakagawa and Tackley, 2004). For actual mantle compositions, effects of relatively minor elements such as Fe and Al should be taken into account, but as we mentioned earlier, these may have opposite effects in modifying the transition pressure which should cancel out each other. Actually, recent experimental results demonstrated that the Pv–PPv transition in peridotitic compositions occurs at pressures close to 120 GPa (Murakami et al., 2005; Ono et al., 2005d). Although a smeared-out transition is expected for this transition when some iron is incorporated in MgSiO_3 (Mao et al., 2004, 2005), these studies on the rock samples indicate that the pressure interval of the mixed phase region of Pv and PPv is not so large, suggesting the occurrence of a sharp boundary (Wyssession et al., 1998). It is also demonstrated that the PPv phase in the peridotite composition is highly magnesium-rich relative to Mw (Murakami et al., 2005), whereas PPv is reported to favor iron compared with Pv in other experimental studies (Mao et al., 2004, 2005; cf. Kobayashi et al., 2005).

Another striking feature of PPv is its elasticity, as predicted by ab initio calculations (Iitaka et al., 2004; Oganov and Ono, 2004; Tsuchiya et al., 2004b). The predicted seismic wave speeds of PPv are slightly faster in V_P and V_S and slower in V_Φ than those of Pv at the transition P , T condition as typically observed at the D'' discontinuities (Lay et al., 2004). These velocity changes across the transition boundary seem to explain the enigmatic anticorrelated anomaly between V_S and V_Φ observed at the bottom of the mantle (Wentzcovitch et al.,

2006; Wookey et al., 2005). Also they can vary with changing the iron and aluminum contents in Pv and PPv (Tsuchiya and Tsuchiya, 2006).

Because of the peculiar crystal structure of PPv, which is highly compressible along the *b* direction, this phase is suggested to be elastically quite anisotropic. The ab initio studies also reported that PPv polycrystalline aggregates with lattice-preferred orientation (LPO) around some crystallographic directions produced by macroscopic stress appear to explain the observed anisotropic propagation of seismic waves in some regions of the D'' layer. In particular, some ab initio studies on high-temperature elasticity (Stackhouse et al., 2005a; Wentzcovitch et al., 2006) showed that the transversely isotropic aggregates of PPv can yield horizontally polarized S wave (SH) which travels faster than vertically polarized S wave (SV) at the lower mantle *P*, *T* conditions, as observed underneath Alaska and central America (Lay et al., 2004). However, the peculiar nature of its shear elasticity suggests that the simple shear motion along the layered structure may not be applicable to the PPv phase at relevant pressures (Tsuchiya et al., 2004b). Moreover, it was predicted that Mw would have substantially large elastic anisotropy under the lower mantle conditions (Yamazaki and Karato, 2002), suggesting that the PPv phase may not be important in producing anisotropic nature in the D'' layer.

The most likely region, where the Pv–PPv transition play important roles in the D'' layer, is probably underneath some of the subduction zones, where the temperatures are expected to be relatively lower than that of the surrounding mantle. In these relatively cold regions in the D'' layer, it is known that a sharp discontinuity exists on the top of this layer, under which the highly anisotropic nature of propagation of SV and SH has also been recognized. If this discontinuity corresponds to the Pv–PPv transition, then one of the most likely features of this transition, that is, its large Clapeyron slope of $dP/dT = 7\text{--}10\text{ MPa K}^{-1}$, suggests that such discontinuity may not exist in warmer regions. For instance, if the temperature in the warmer region is higher than the cold areas by several hundred degrees (such a lateral temperature variation is very likely to exist in the CMB region), this transition would occur in the middle of the D'' layer. However, as the temperature is expected to increase sharply toward the CMB within the D'' layer, the geotherm in the warmer region may not cross the Pv–PPv phase boundary as illustrated in Figure 12, although some seismological observations would suggest not so high CMB temperatures in most regions of the lower mantle (Kawai and Tsuchiya, 2009). In contrast, it is interesting to see that there is a possibility that the geotherm in the colder region might cross the boundary twice, as suggested by recent computational modeling (Hernlund et al., 2005; Wookey et al., 2005).

Thus, if the transition pressure and the Clapeyron slope of the Pv–PPv transition predicted by ab initio calculations are correct, many of the observed features in the CMB region can be explained. In warmer regions such as underneath Hawaii or South Africa, this transition would not have any significant role in producing the peculiar features, such as the presence of an ultra-low velocity region or a large low velocity structure in these regions, which should be attributed to other phenomena, such as partial melting of the D'' layer material or chemical changes (e.g., Lay et al., 2004). Reactions between Mg–Pv in the

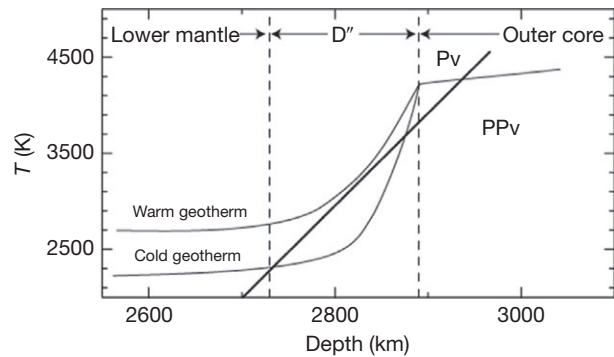


Figure 12 A schematic illustration of the plausible thermal structure at the bottom of the lower mantle, where a steep temperature gradient should be realized due to the formation of the thermal boundary layer. Only the sub-adiabatic cold geotherm may cross the Pv–PPv phase boundary, and the PPv phase may be sandwiched by Pv because of the shallow slope of this transition and the sharp temperature increase in this region. Reproduced from Hernlund JW, Thomas C, and Tackley PJ (2005) A doubling of the post-perovskite phase boundary and structure of the Earth's lowermost mantle. *Nature* 434: 882–886.

warm regions with liquid iron may produce an iron-rich PPv phase in these regions, which could also contribute to the observed low velocities in these regions, as suggested by Mao et al. (2005). Such reactions between Pv (or PPv) and molten iron should be further explored experimentally to address the nature of the (ultra-) low velocity zones within the D'' layer.

Over the past 30 years, the lowermost part of the Earth's mantle, the D'' layer, has been recognized as being a seismological anisotropic structure, whereas the rest of the lower mantle is nearly isotropic (Kendall and Silver, 1996; Mitchell and Helmberger, 1973; Panning and Romanowicz, 2004; Vinnik et al., 1998). Several observations suggest that the horizontally polarized shear wave (V_{SH}) is faster than the vertically polarized shear wave (V_{SV}) in most areas of the D'' layer (Kendall and Silver, 1996; Vinnik et al., 1998) except beneath the Africa and Pacific low-velocity provinces (Panning and Romanowicz, 2004). Several scenarios have been proposed for the splitting mechanism of the polarized shear waves in the D'' layer. One is the formation of shape-preferred orientations due to the alignment of fluid-inclusion or anisotropic atomic diffusion (Mainprice et al., 2000). Another, more efficient, origin can be found in the development of the LPO of (Mg,Fe)-PPv, which is thought to be the most abundant mineral in the D'' layer (Tsuchiya et al., 2004a) with a strong elastic anisotropy (Tsuchiya et al., 2004b), during plastic deformation with anisotropic shear response of the slip systems, such as dislocation creep or mechanical twinning. Although several high-pressure experiments have been performed to understand the plastic deformation mechanism of PPv (Hirose et al., 2010; Merkel et al., 2007; Miyagi et al., 2010, 2011; Okada et al., 2010), results are still largely controversial primarily due to experimental difficulty in determining the stable slip plane (Merkel et al., 2007; Miyagi et al., 2010). Most of these deformation experiments were conducted at room temperature, which is far lower than the geophysically relevant temperature of the D'' region of $\sim 2500\text{--}3800\text{ K}$ (Brown and Shankland, 1981; Kawai and Tsuchiya, 2009). However, a high-temperature deformation experiment (Hirose et al., 2010) also shows the (001) plane as the stable slip plane of PPv. This slip mechanism can explain the

$V_{SH} > V_{SV}$ type polarization anisotropy observed in the D'' layer (Tsuchiya et al., 2004b).

Some theoretical studies also suggested contradicting results regarding the (100) or (110) slip planes (Oganov et al., 2005b) and (010) (Carrez et al., 2007) for PPv, primarily because these examined only particular structure modifications or calculated the GSF energies of limited slip planes. Another work of Fe-bearing Mg-PPv, on the other hand, calculated the GSF of several slip systems (Metsue and Tsuchiya, 2013) and found that pure and Fe-bearing $MgSiO_3$ PPv should demonstrate similar LPO patterns with a strong signature of the [100] (001) slip system. Note again that an aggregate with this deformation texture is expected to produce a $V_{SH} > V_{SV}$ type polarization anisotropy, being consistent with seismological observations.

2.03.6 Summary

Recent advances in both experimental and computational techniques have enabled the quantitative study of phase transitions and mineral physics properties under the lower mantle P , T conditions. Although uncertainties in pressure and temperature are of the order of $\sim 10\%$ of the nominal values in typical experiments of LHDAC, this apparatus can now produce pressures and temperatures equivalent to those of the center of the Earth. In contrast, pressures available in KMA have long been limited to ~ 30 GPa in spite of its superiority in the accuracy of P , T measurements over LHDAC. However, recent developments in KMA using SD anvils expanded this pressure limit to the Mbar region, allowing detailed mineral physics studies down to the middle part of the lower mantle.

The accuracy of the mineral physics studies based on ab initio calculations has also been dramatically improved in the last decade. A variety of methods and techniques have been developed for the practical applications of DFT to mineral physics studies at very high pressure and temperature. As a result, remarkable agreements among the results from different research groups have been obtained for the phase transition pressures, elastic properties, etc., of some high-pressure phases under the lower mantle pressures. Thus, such mineral physics properties of high-pressure phases in the lower mantle can now be evaluated and cross-checked on the basis of the independent experimental studies using LHDAC and KMA and of ab initio calculations.

Phase transitions in major and minor minerals relevant to the mantle and subducted slabs have been studied by using the above independent methods, which clarified structural phase transitions in most of these minerals at pressures and temperatures characteristic of the lower mantle, although there remain some controversial results on the phase transition pressures, their temperature dependencies, element partitioning among the coexisting phases, etc. Although the elastic properties of high-pressure phases, particularly shear properties, have not been well documented under the lower mantle conditions, EoS parameters of some of these phases have successfully been determined by a combination of synchrotron source and KMA-LHDAC or by ab initio methods. Thus, the density changes in representative mantle and slab compositions can

be accurately evaluated on the basis of the thermoelastic data on individual high-pressure phases and mineral proportion changes in these compositions.

The 660 km discontinuity has conventionally been interpreted in terms of the spinel–postspinel phase transition in Mg_2SiO_4 . However, results of the recent experimental, seismological, and geodynamics studies do not seem to be totally consistent with this interpretation. The presence of either a basaltic or a harzburgite layer, as a result of accumulation of subducted slab materials, may explain such inconsistency and the complex structure near the 660 km discontinuity. The validity of this and other classes of mineralogical models relevant to the origin of the 660 km discontinuity can be evaluated on the basis of mineral physics tests, when accurate elastic wave velocity data are accumulated for the pyrolite, harzburgite, MORB, and other subducted materials under the P , T conditions corresponding to these depths.

The middle part of the lower mantle is believed to be generally homogeneous in both mineralogy and chemistry, as compared with those in the uppermost and lowermost parts of the lower mantle. No major phase transitions are expected to occur in the subducted slab lithologies and the surrounding mantle under the P , T conditions of this part of the lower mantle, except for the rutile to $CaCl_2$ transition in SiO_2 and electronic spin transitions in Mw and Pv. The seismic scatterers of presumably flat bodies found in the middle part of the lower mantle should be related to this phase transition in the former subducted oceanic crust, which may subduct into the deep lower mantle once it passes the density crossover near the 660 km discontinuity. Thus, some parts of the basaltic component of the slab may ultimately reach the bottom of the lower mantle because of its higher density relative to the mantle materials throughout the lower mantle. In contrast, a harzburgite-rich layer may be present around the 660 km discontinuity as a result of accumulation of main bodies of stagnant slabs in this region. However, as the density difference between this layer and the surrounding mantle is not large, thermal effects should be predominant over the chemical effects in gravitational stability of such a layer, leading to possible generation of plumes in the region.

The Pv–PPv transition should have significant implications for the structure, properties, and dynamics of the D'' layer. Some properties, such as Clapeyron slope, transition pressure, elastically anisotropic nature, and density increase relevant to the Pv–PPv transition seem to be consistent with the seismologically observed signatures in some regions of the D'' layer. Further detailed and more accurate experimental studies on this transition are required based on independent techniques using KMA or LHDAC with improved accuracy, in addition to the theoretical studies, to understand the nature of this region of the lower mantle.

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2.04 Mineralogy of the Earth: Trace Elements and Hydrogen in the Earth's Transition Zone and Lower Mantle

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2.04.1 Introduction

The aim of this chapter is to review the available experimental and theoretical evidence bearing on the distribution of trace elements and H in the transition zone and lower mantle. The first step, before considering the processes involved in the chemical differentiation of the Earth, is to consider the available constraints on the bulk composition of the silicate Earth.

2.04.1.1 Concentrations in the Primitive Upper Mantle and Bulk Silicate Earth

The silicate Earth is conveniently divided into continental crust (0.55% by mass), oceanic crust (0.15%), upper mantle (15.3%), transition zone (11.1%), and lower mantle (72.9%). The compositions of continental and oceanic crust are consistent with ultimate derivation from the mantle (Hofmann, 1988) by processes of near-anhydrous partial

melting at mid-ocean ridges and more H₂O-rich melting above subduction zones (Tatsumi and Eggins, 1995). In order to estimate the composition of the bulk silicate Earth, therefore, we need to reconstruct the composition of the mantle prior to extraction of the crust. This is normally done using the compositions of fertile or least fractionated upper-mantle peridotites (e.g., Allègre et al., 1995; Jagoutz et al., 1989; McDonough and Sun, 1995; Palme and O'Neill, 2003; Walter, 2003), which occur as xenoliths in volcanic rocks and in orogenic massifs. Garnet peridotite xenoliths in kimberlites and lamproites sample the deepest levels, up to about 200 km below the continental crust (e.g., Rudnick and Nyblade, 1999). This procedure yields the concentrations of a wide range of elements in the primitive (i.e., undifferentiated) upper mantle. It is most accurate for those elements that are either compatible in mantle silicates (partition strongly into the solid during partial melting) or only slightly incompatible. The concentrations of highly incompatible elements, which are concentrated strongly into the crust, are more accurately determined from the crustal rocks themselves. It should be noted that this primitive upper mantle (PUM) does not correspond to the source region of mid-ocean ridge basalts (MORBs). The latter is more depleted in incompatible elements such as K, U, Th, and the light rare earth elements (REEs).

Having estimated the composition of the PUM, it is important to establish any clear compositional differences between this part of the mantle and the inaccessible deeper parts. To do this, it is necessary to have a model for the bulk composition of the Earth. Chemical affinities between Earth, Moon, Mars, Mercury, Vesta, and chondritic meteorites imply that these meteorites are a suitable reference point for the compositions of terrestrial planets (e.g., Morgan and Anders, 1980; Ringwood, 1979; Wänke and Dreibus, 1988; Wasson, 1988). CI carbonaceous chondrites in particular have strong compositional similarities to the solar photosphere (e.g., Palme and Jones, 2003, and references therein) and appear to represent

primitive planetary material, with the exceptions that they are volatile-enriched relative to the terrestrial planets and volatile-depleted relative to the sun.

Figure 1 shows the estimated composition of the PUM plotted as a function of the temperature by which 50% of the element of interest would have condensed during cooling of a gas of solar composition (Lodders, 2003; Wasson, 1985). The most important point is that refractory lithophile elements (RLEs) such as Ca, Sc, Ti, Zr, U, and the REEs are present in the PUM in approximately the same relative proportions as in carbonaceous chondrites (e.g., McDonough and Sun, 1995). The implication is that the bulk Earth contains the same relative proportions of refractory elements as the carbonaceous chondrites. This is the basis of the (carbonaceous) chondrite reference model. Furthermore, since RLEs are not fractionated from one another in Earth's PUM, one important consequence of choosing a chondritic reference is that the core, lower mantle, and transition zone do not have fractionated RLE patterns either. The composition of the PUM has therefore been considered for many elements to be representative of the composition of the bulk silicate Earth.

As can be seen on the left-hand side of Figure 1, there is a decreasing relative abundance of some lithophile elements in the silicate Earth with decreasing condensation temperature or increasing volatility. This demonstrates that the silicate Earth is depleted in volatile elements (e.g., Li, B, Na, K, and Rb) with respect to the chondritic reference. Depletions of the silicate Earth in refractory 'siderophile' elements such as W, Mo, Au, Re, and platinum-group elements are likely due to partial extraction of these elements into the core. Some of the more volatile elements such as S, Se, Pb, Ge, and P fall well below their expected positions on the 'volatility trend' of Figure 1 and are also assumed to be partially present in the core.

The concentrations of hydrogen species (not plotted in Figure 1 due to their extremely high volatility) in the depleted upper mantle can be approximated from corresponding

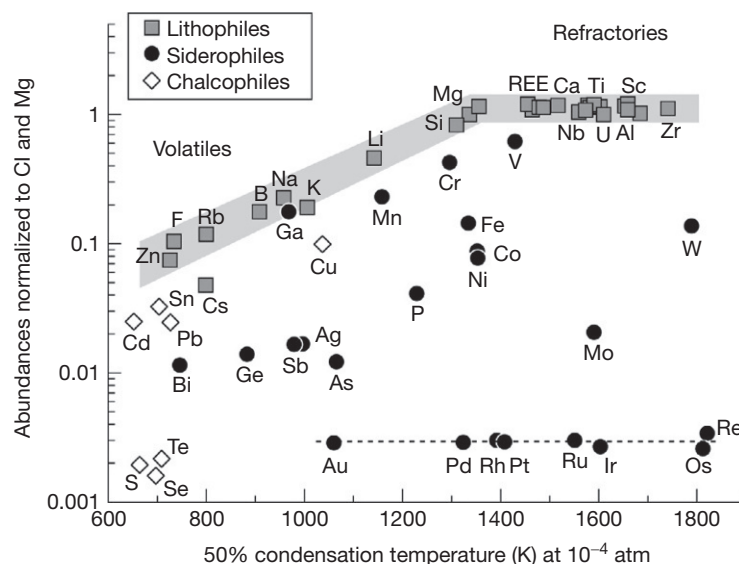


Figure 1 Elemental abundances in the primitive upper mantle (PUM) normalized to CI carbonaceous chondrite and Mg (=1.0) plotted relative to 50% condensation temperature at 10^{-4} atm pressure, which is used as a proxy for a nebular condensation sequence. Data for condensation temperatures are from Lodders (2003); chemical data for chondrites are from Wasson and Klemmeyn (1988) and for the PUM from McDonough (2001).

abundances in MORB glasses, while those in the whole mantle may be estimated from geochemical arguments such as those in the preceding text (Wänke and Dreibus, 1988) and the K/H ratio of the crust plus hydrosphere (Jambon and Zimmermann, 1990). If we consider N-MORBs, which come from upper-mantle sources depleted in incompatible elements, then, assuming 10% melting, the source regions contain 80–180 ppm by weight of H₂O. For the more enriched source of E-MORBs, mantle water contents of 200–950 ppm are inferred, while basalts from back-arc basins are products of source regions containing around 1000–3000 ppm of H₂O (Michael, 1988, 1995; Sobolev and Chaussidon, 1996). Jambon and Zimmermann (1990) argued that the bulk silicate Earth water content (including crust and hydrosphere) is in the 550–1900 ppm range with the lower bound corresponding to the oceans plus the water concentration in the MORB source and the upper bound coming from the assumption that the K₂O/H₂O ratio of crust plus oceans (0.14) applies to the bulk silicate Earth. In the former case, current water concentrations in the whole mantle would be similar to those for the MORB source region (~200 ppm) and would correspond reasonably well to those derived from cosmochemical arguments (Wänke and Dreibus, 1988). In the latter case, the mantle would currently contain about 1500 ppm water, and the implication is that there is a water-rich reservoir in either the transition zone (e.g., Bercovici and Karato, 2003) or the lower mantle (e.g., Murakami et al., 2002). Geochemical arguments suggest that the source regions of ocean island basalts (OIBs) are water-rich, with water contents between 300 and 1000 ppm (e.g., Dixon and Clague, 2001). Assuming that the sources of plumes reside in the deep mantle, this provides further evidence for a water-rich deep mantle.

Although there are considerable uncertainties in the concentrations of H species in the mantle, particularly below 410 km depth, geochemical arguments indicate that these concentrations in both upper and lower mantles are well below 1 wt.% so that they are unlikely to affect the elastic properties or density of the mantle except where conditions are close to the solidus. However, they have impacts (1) on the transport properties of minerals (diffusion, deformation, and electrical conduction), with implications for mantle viscosity and convection and seismic anisotropy, (2) on the differentiation processes (melting behavior of mantle rocks and metasomatism), and (3) on the properties of the seismic discontinuities.

2.04.1.2 Differentiation of the Silicate Earth and Formation of Deep-Mantle Reservoirs

To study the distribution of trace elements and H in the deep mantle, it is helpful to know which mineralogical structures/reservoirs inherited from planetary differentiation are potentially present in the mantle. During its early history, it is probable that the Earth underwent extensive melting due to the impact energy of planetesimal bombardment, the heat produced by decay of short-lived radiogenic isotopes, and the gravitational energy of core segregation (e.g., Chambers, 2004; Wetherill, 1990). Melting may have been long-lived and represented by a deep vigorously convecting magma ocean (e.g., Abe, 1997; Ohtani, 1985). Upon cooling, the

magma ocean would have gradually crystallized, leading, in principle, to a fractionally crystallized mantle. Many previous studies have considered 'bottom-up' crystallization, that is, magma ocean crystallization beginning at the base of the mantle (e.g., Abe, 1997; Miller et al., 1991; Solomatov, 2000; Walter and Tronnes, 2004). More recent studies suggest that crystallization is likely to have commenced in the mid-mantle, leading to two residual liquids, at the base of the mantle and near surface (e.g., Labrosse et al., 2007; Stixrude et al., 2009) with significant mantle stratification. Although convection may have significantly reduced such stratification (Solomatov, 2000; Tonks and Melosh, 1993), segregation of large amounts of deep-mantle liquidus minerals such as majoritic garnet, magnesium silicate perovskite, and calcium silicate perovskite would likely have driven element concentrations away from the initial primitive mantle values. Mantle degassing of volatile species (H, C, N, O, and noble gases) and closure of the atmosphere took place soon after accretion ceased (e.g., Allègre et al., 1986).

Until recently, the lack of accurate crystal–liquid partition coefficients under deep-mantle conditions has limited the ability to model properly the chemical differentiation of a molten silicate Earth. Estimated compositions of the PUM are consistent with a whole mantle of homogeneous composition at least for RLEs. Qualitatively, this implies either that the mantle did not differentiate early in Earth history or that subsequent solid-state convection in the mantle erased any initial stratification (e.g., van Keken et al., 2002). We will investigate the possibility of stratification further in Section 2.04.2.4.3. Another possible mechanism of fractionation is segregation of melts denser than the solid mantle to produce a compositionally distinct 'layer' in the deep mantle. This will also be addressed in Section 2.04.2.4.3. The existence of large-scale heterogeneities in the transition zone and lower mantle is supported by geochemical arguments, which suggest the presence in the deep mantle of undegassed reservoirs enriched in radiogenic heat-producing elements and with subchondritic ¹⁴²Nd/¹⁴⁴Nd ratio (e.g., Allègre et al., 1996; Becker et al., 1999; Boyet and Carlson, 2005; Kellogg et al., 1999; Samuel and Farnetani, 2003; Turcotte et al., 2001).

2.04.1.3 Objectives

The aim of this work is to provide a summary of experimental constraints on the distribution of trace elements in the transition zone and lower mantle, with a particular emphasis on RLEs and the volatile species of H. We will start by briefly describing theoretical methods of systematizing the incorporation of trace elements in deep-mantle minerals as a function of ionic radius and cation charge. Together with a review of recent experimental results on deep-mantle minerals, we will discuss the effects of crystal structure, composition, pressure, and temperature on trace element partitioning. This will allow us to describe the implications of deep-mantle melting for the distribution of trace elements in the transition zone and lower mantle. The second part of this chapter will focus on the distribution of water in the transition zone and lower mantle.

As discussed earlier, available samples of mantle rocks are limited to the uppermost mantle (<~200 km in depth). Studies of mineral inclusions in 'deep' diamonds have, however,

provided additional insights into the geochemistry and mineralogy of the deep mantle. The results tend to confirm conclusions obtained from high-pressure experimental studies and will not be discussed in detail here. Readers seeking further information on inclusions in diamonds are advised to begin with the reviews by Harte et al. (1999) and Stachel et al. (2004).

2.04.2 Crystal–Melt Partition Coefficients and Controlling Factors

In order to understand the distribution of trace elements and volatiles in the silicate Earth, it is first necessary to consider how they dissolve in the minerals of the mantle. As shown in Figure 2, if we assume that the whole mantle is approximately the same major element composition as upper-mantle peridotite, then the principal mineral phases are magnesium silicates and oxides – olivine, orthopyroxene, and garnet in the upper mantle; majoritic garnet, wadsleyite [β -(Mg,Fe) $_2$ SiO $_4$], and ringwoodite [γ -(Mg,Fe) $_2$ SiO $_4$] in the transition zone; and magnesium silicate perovskite and ferropericlase in the lower mantle. It must be noted that, in addition to garnet and orthopyroxene, Ca dissolves in two other mineral phases: clinopyroxene in the upper mantle and calcium silicate perovskite in the lower mantle. The distribution of elements between these phases depends, of course, on the chemical properties of the elements of concern and the crystallochemical properties of the phases themselves. Since fractionation of elements between one part of the Earth and another (e.g., mantle–crust or upper mantle–lower mantle) almost invariably takes place

through processes of melting and crystallization, it is convenient to consider element distributions in terms of partitioning between solids and melts.

Recent work on solid–melt partitioning of cations (Blundy and Wood, 1994; Wood and Blundy, 2001) has quantified the effects of the ionic radius and charge on partitioning behavior. Blundy and Wood (1994) showed, following elastic strain theory (Brice, 1975), that the solid–liquid partition coefficient of ion i of radius r_i (D_i) can be calculated from that (D_o) of an ion of the same charge that enters the site without strain as follows:

$$D_i = D_o \exp \left(\frac{-4\pi E_s N_A}{RT} \left(\frac{r_o}{2} (r_o - r_i)^2 - \frac{1}{3} (r_o - r_i)^3 \right) \right) \quad [1]$$

In eqn [1], r_o is the effective radius of the site, N_A is Avogadro's number, and E_s is the effective Young's modulus of the site. Equation [1] describes a near-parabolic relationship between D_i and ionic radius for ions of fixed charge with the peak of the parabola corresponding to r_o and D_o and the tightness of the parabola depending on the 'stiffness' of the site represented by E_s . Partition coefficient D_i is defined as the ratio of weight concentration of element i in crystal phase to the weight concentration of element i in the liquid phase.

2.04.2.1 Majoritic Garnet

2.04.2.1.1 Crystallochemical control

Garnets have cubic symmetry with the general structural formula $X_3Y_2Z_3O_{12}$, where the X-, Y-, and Z-positions are dodecahedral, octahedral, and tetragonal cation sites, respectively (e.g., Heinemann et al., 1997). Majoritic garnets are rich in MgSiO $_3$ component, which means that Mg is present in both X- and Y-sites, while Si occupies both Y- and Z-sites. Al and Fe $^{3+}$ almost certainly occupy the Y-site, while Ca and Fe $^{2+}$ occupy the X-site. Corgne and Wood (2004) had shown that crystal–melt partition coefficients for a suite of isovalent cations entering either the X- or Y-site of majoritic garnet exhibit the near-parabolic dependence on the radius of the incorporated cations predicted from eqn [1] (see Figure 3; Corgne and Wood, 2004). This underlines the important contribution made by the crystal structure to the control of trace element partitioning. Furthermore, as previously found for clinopyroxene and low-pressure garnet (Hill et al., 2000; Van Westrenen et al., 2000), Young's modulus E_s increases and optimum radius r_o decreases with increasing charge of the cation incorporated at the X-site of majoritic garnet. In constructing Figure 3, Corgne and Wood (2004) considered that each ion enters only one site, with the exception of Mg and Si for which individual partition coefficients for the X- and Y-sites are reported. All ions with radius greater than that of Mg were allocated to the large X-site and all ions close to Al in size to the Y-site. This leaves a few ions, notably Ni, Sc, Ga, Cr, Ti, Sn, Hf, and Zr, which may, like Mg, enter both X- and Y-sites. Comparison of measured partition coefficients for these elements with the parabolas based on other elements suggests that Cr, Ga, and Ti predominantly enter the Y-site, while Sn, Hf, and Zr enter the X-site (Figure 3). Similarly, P and B may, like Si, enter both Y- and Z-sites. D values for divalent transition metals do not fit the trend predicted from the elastic strain

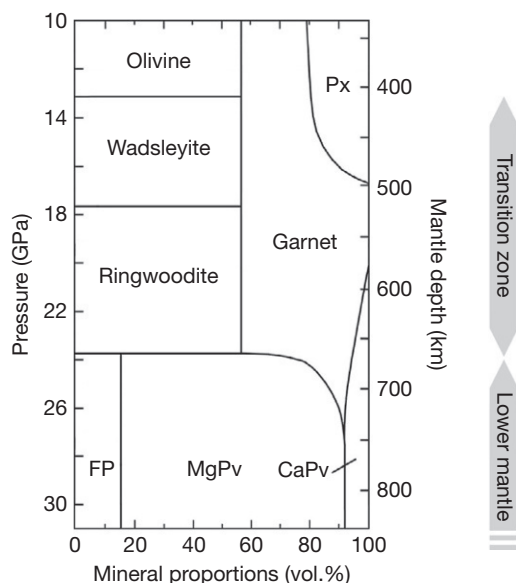


Figure 2 Mineral proportions in peridotite mantle composition as a function of pressure or depth. Symbols used are Px, pyroxene; FP, ferropericlase; MgPv, magnesium silicate perovskite; and CaPv, calcium silicate perovskite. Modified from Ringwood AE (1991) Phase transformation and their bearing on the constitution and dynamics of the mantle. *Geochimica et Cosmochimica Acta* 55: 2083–2110; Irifune T (1994) Absence of an aluminous phase in the upper part of the Earth's lower mantle. *Nature* 370: 131–133.

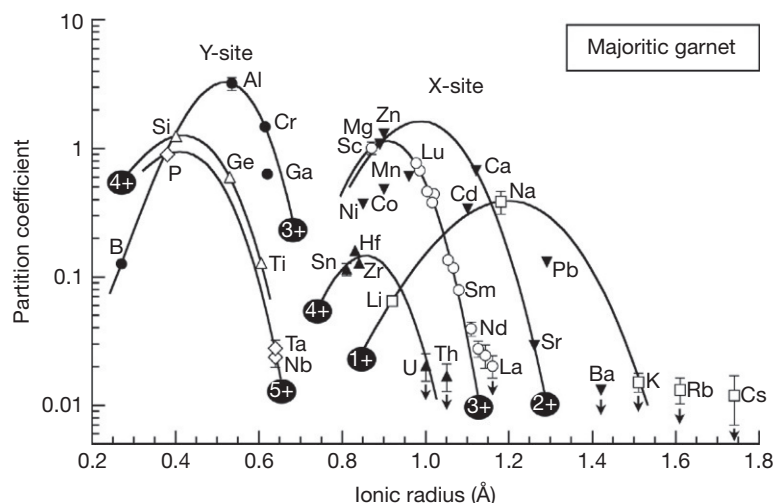


Figure 3 Partition coefficients for elements entering the X- and Y-sites of majoritic garnet as a function of ionic radius. Parabolas are fits of eqn [1] to experimental data. Partition coefficients for U, Th, La, Ba, K, Rb, and Cs are upper bounds. Reproduced from Corgne A and Wood BJ (2004) Trace element partitioning between majoritic garnet and silicate melt at 25 GPa. *Physics of the Earth and Planetary Interiors* 143–144: 407–419.

model applied to Ca, Mg, and Sr. These anomalies probably reflect both crystal field effects (for Ni and Co) and variable valence (for Fe, Cr, and perhaps Mn). The anomalous behavior of Pb^{2+} is also generally observed (e.g., Blundy and Wood, 1994) and probably due to the presence of a lone pair of electrons on this ion.

2.04.2.1.2 Effects of pressure, temperature, and composition

Trace element partitioning must, in general, depend on pressure and temperature because partitioning from melt to crystal involves changes in fundamental thermodynamic properties of the species of concern. In addition to these fundamental effects, there are ‘pressure effects’ arising from changes in crystal composition as pressure and temperature are increased. For example, in the shallow mantle, garnets have high concentrations of the pyrope ($\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$) component. At greater depths, as pressure and temperature increase, the Al content of the garnet decreases and the phase becomes richer in majorite ($\text{Mg}_4\text{Si}_4\text{O}_{12}$) component (e.g., Irfune, 1987). As a result, trace element partitioning should change with pressure and temperature for both fundamental thermodynamic reasons and due to changes in crystal chemistry. Figure 4 presents a series of partitioning parabolas obtained over a wide range of pressure conditions (3–25 GPa). Data at 3 GPa from van Westrenen et al. (2000) in the $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-FeO}$ system ($\text{Py}_{78}\text{Gr}_{19}\text{Alm}_9$ garnet with Mg# of 89) are compared with data from Draper et al. (2003) obtained at 9 GPa on an ordinary chondrite composition ($\text{Py}_{80}\text{Gr}_{17}\text{Alm}_3$ garnet with Mg# of 83), with data from Walter et al. (2004) obtained at 23.5 GPa on a fertile peridotite composition (garnet Mg# of 95), with data from Corgne and Wood (2004) at 25 GPa on an Al-, Fe-rich peridotite composition (garnet Mg# of 89), and with data from Corgne et al. (2012) obtained at 10, 15, and 17 GPa on a primitive mantle model composition with chondritic Mg/Si (garnet Mg# 94–96). As observed by Draper et al. (2003), between 5 and 9 GPa at approximately constant temperature ($\sim 1800^\circ\text{C}$), D_o^{3+} and E_X^{3+} for the X-site decrease with

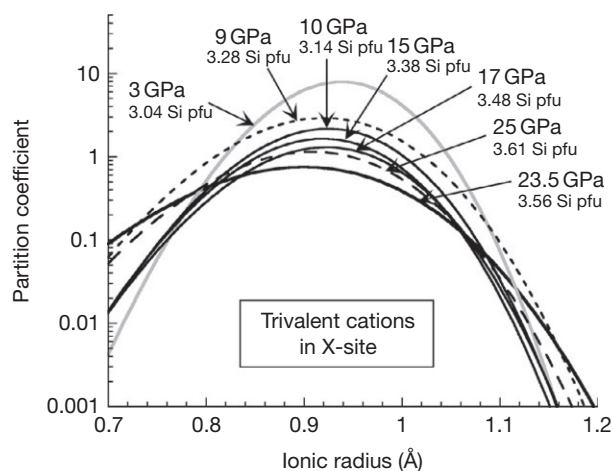


Figure 4 Lattice strain parabolas for trivalent cations (REE, Y, and Sc) entering the X-site of majoritic garnet. As observed at low pressures (Draper et al., 2003), D_o^{3+} decreases with increasing pressure, that is, with increasing majorite component (quantified using number of Si atoms per formula unit, Si pfu). References are van Westrenen et al. (2000), 3 GPa and garnet Mg# of 89; Draper et al. (2003), 9 GPa and garnet Mg# of 83; Corgne et al. (2012), 10–17 GPa and garnet Mg# of 94–96; Walter et al. (2004), 23.5 GPa and garnet Mg# of 95; and Corgne and Wood (2004), 25 GPa and garnet Mg# of 89. See text for complete discussion of controlling factors.

increasing pressure, that is, with increasing majorite component. Considering a wider range of pressure (Figure 4), D_o^{3+} decreases by about an order of magnitude from 8 at 3 GPa to 0.8 at 25 GPa. Furthermore, although there are relatively large uncertainties in D 's for light REE, an increase of pressure results in more open parabolas, corresponding to lower values of Young's modulus (E_X^{3+}). In other words, the X-site becomes ‘softer,’ that is, more elastic, with increasing pressure and increasing majorite component.

Although the changes in D values shown in Figure 4 are nominally due to pressure, it must be emphasized that

temperature and compositional changes cannot be separated from those of pressure. Experiments at progressively higher pressure involve progressively higher temperatures and higher majorite contents of the resultant garnets. Thus, for example, one could envisage that the decrease of D_o^{3+} with increasing pressure (Figure 4) is not directly due to pressure but rather due to the increasing incorporation of Si^{4+} at the Y-site in the garnet. Increasing replacement of Al^{3+} by Si^{4+} could be expected to make it more difficult to charge-compensate the substitution of Mg^{2+} by $3+$ ions at the X-site and hence lead to decreasing D_o^{3+} for this site. The interrelationships between pressure, temperature, and composition mean, therefore, that selection of partition coefficients for majoritic garnets must be performed cautiously and preferably by interpolation of values measured for bulk compositions closely corresponding to the ones of interest.

2.04.2.1.3 Partitioning models for garnet

In the last decade, van Westrenen and coworkers have developed equations describing partitioning of REE, Sc, and Y between garnet and anhydrous silicate melts (Draper and van Westrenen, 2007; van Westrenen and Draper, 2007), which take full account of pressure, temperature, and bulk garnet composition. With the recent refinement proposed by Corgne et al. (2012), both models proposed by Draper and van Westrenen (2007) and van Westrenen and Draper (2007) can be used to predict garnet–melt partitioning of large trivalent cations at pressures to 25 GPa. The following equations combined with the lattice strain model (eqn [1]) are used for modeling:

$$r_o(\text{\AA}) = 0.9302 X_{Py} + 0.993 X_{Gr} + 0.916 X_{Alm} + 0.946 X_{Spes} \\ + 1.05 (X_{And} + X_{Uv}) - 0.0044(\pm 3) (P - 3) \\ + 0.000058(\pm 7)(T - 1817)$$

$$E_s(\text{GPa}) = 2826(\pm 174) (1.38 + r_o)^{-3} + 12.4(\pm 13)P \\ - 0.072(\pm 7) T + 237(\pm 8)(Al + Cr)_{apfu}$$

$$D_o(1) = 3.24(\pm 146) K_D^{[Fe-Mg]} + 3.01 (\pm 20) D_{Mg} \\ - 2.59(\pm 104)$$

$$D_o(2) =$$

$$\exp \left[\frac{389500(\pm 6040) + 7850(\pm 1160)P - 110(\pm 42)P^2 - 218(\pm 7)T}{RT} \right] \\ / (\gamma_{Fe} D_{Fe})^2$$

In these equations, T is temperature in K, P is pressure in GPa, X is mole fraction, Py=pyrope ($Mg_3Al_2Si_3O_{12}$), Gr=grossular ($Ca_3Al_2Si_3O_{12}$), Alm=almandine ($Fe_3Al_2Si_3O_{12}$), Spes=spessartine ($Mn_3Al_2Si_3O_{12}$), And=andradite ($Ca_3Fe_2Si_3O_{12}$), Uv=uvavovite ($Ca_3Cr_2Si_3O_{12}$), $(Al + Cr)_{apfu}$ is the number of atoms per formula unit (12 oxygens) of Al and Cr in garnet, $K_D^{[Fe-Mg]}$ is the exchange coefficient of Fe–Mg between garnet and melt, D_{Mg} and D_{Fe} are Mg and Fe garnet–melt partition coefficients, γ_{Fe} is the activity coefficient of Fe in garnet, and uncertainties are one sigma error. $D_o(1)$ is the semiempirical expression derived by Draper and van Westrenen (2007), whereas $D_o(2)$ is the thermodynamic expression initially derived by van Westrenen and Draper (2007) and refined by Corgne et al. (2012).

2.04.2.2 Magnesium Silicate Perovskite

As shown in Figure 2, in a peridotitic mantle composition, magnesium silicate perovskite forms from the breakdown of ringwoodite at 24 GPa and from the gradual decomposition of majoritic garnet between 24 and 27 GPa. Assuming that the lower mantle is peridotitic, it is made up, by weight, of ~79% (Mg, Fe)SiO₃ perovskite (MgPv), 16% (Mg, Fe)O ferropericlasite (FP), and 5% CaSiO₃ perovskite (CaPv) (e.g., Wood, 2000). The perovskite phases are crystallochemically unusual because of the presence of Si^{4+} in octahedral coordination (B-site), while the larger cation site (A-site) is regular 12-coordinate in CaPv and distorted 12-coordinate (with eight close oxygens) in MgPv. When crystallized from peridotitic compositions at high temperatures, MgPv contains ~4 wt.% Al₂O₃ (Liebske et al., 2005), while the alumina content of coexisting calcium perovskite is substantially less (Wood, 2000). Dissolution of alumina into MgPv has a dramatic effect on the properties of this phase, particularly on the oxidation state of the iron it contains. Al^{3+} prefers to replace Si^{4+} on the octahedral site and this is coupled, in Fe-bearing perovskites, to replacement of Mg^{2+} by Fe^{3+} (Wood and Rubie, 1996). The component $Fe^{3+}AlO_3$ is so stable in solution (Frost and Langenhorst, 2002; McCammon et al., 1997) that it can force the disproportionation of ferrous iron into ferric iron plus metal (Frost et al., 2004), and its stability means that ~60% of the iron present in lower-mantle Al-bearing (Mg, Fe)SiO₃ perovskite should be Fe^{3+} . Clearly, coupled substitutions of this type may also affect the partitioning of other highly charged elements into perovskite.

Recent experimental and analytical improvements have made it possible to generate accurate MgPv–melt partition coefficients for a large number of trace elements. Since MgPv is believed to be the most abundant mineral in the mantle, these technical advancements are critical to the understanding of trace element distributions in the Earth. Hereafter, we summarize results from recent experimental studies at 23.5–26 GPa (Corgne et al., 2005; Liebske et al., 2005; Walter et al., 2004) that constrain factors controlling MgPv–melt partitioning.

2.04.2.2.1 Crystal chemistry

As illustrated earlier for majoritic garnet, MgPv–melt partition coefficients can be parameterized using the ‘lattice strain’ model (eqn [1]). An example of lattice strain fits for MgPv–melt partition coefficients of elements entering the A-site is given in Figure 5. Note that because ionic radii for 12-fold coordination are not available for most elements, values corresponding to an eightfold coordinated site were used. These are ~0.2 Å smaller (Shannon, 1976). The successful application of the lattice strain theory confirms that crystal structure makes an important contribution to MgPv–melt partitioning. However, the partitioning behavior of some elements, notably transition elements, Pb, Ce, and Ba, is poorly modeled by the lattice strain theory. This indicates that additional factors such as crystal field effects or multiple valency complicate MgPv–melt partitioning of transition metals. For example, as shown in Figure 6, D_{Ce} is greater than predicted from the ‘3+ parabola.’ Liebske et al. (2005) suggested that this is the result of some Ce being present as Ce^{4+} . Ba also has a

partition coefficient higher than predicted from the lattice strain model. Based on the observation that Ba^{2+} has an ionic radius similar to O^{2-} , Walter et al. (2004) suggested that Ba^{2+} partly substitutes for O^{2-} and that charge compensation occurs by formation of a Si^{4+} vacancy.

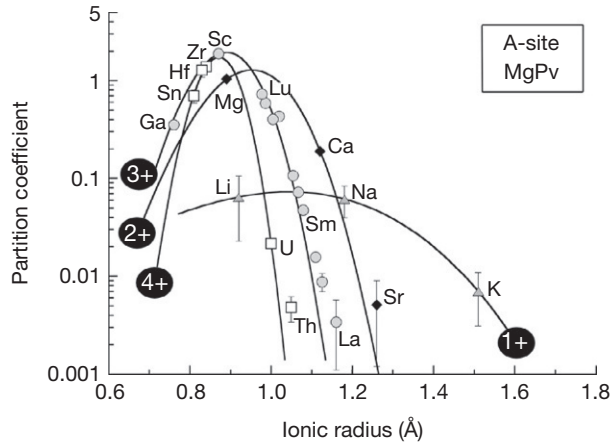


Figure 5 Partition coefficients for element entering the A-site of magnesium silicate perovskite (MgPv) as a function of ionic radius. Parabolas are fits of eqn [1] to experimental data from Corgne et al. (2005). In this case, MgPv contains 1.9 wt.% Al_2O_3 and 3.0 wt.% 'FeO'. Partition coefficients for divalent transition metals, Pb^{2+} , Ba^{2+} , and Ce^{3+} , are not shown because of effects in addition to lattice strain (see text for discussion). Ionic radii are values for an eightfold coordinated site taken from Shannon (1976), as no consistent set of 12-fold coordinated radii exists.

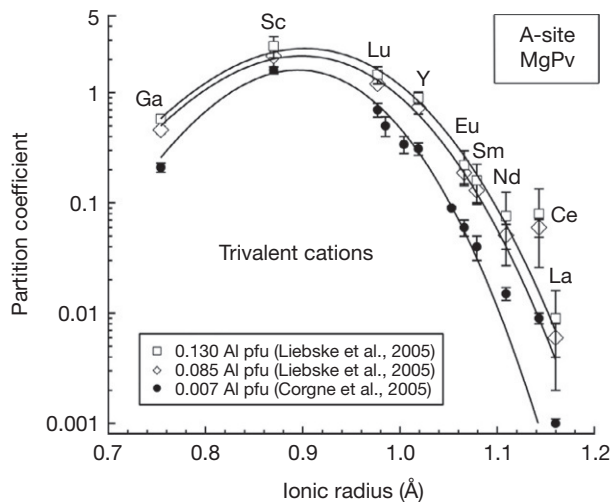


Figure 6 MgPv-melt partition coefficients for trivalent elements and fits to eqn [1] as a function of cation radius. Note that D_{Ce} plots higher than predicted probably because of some Ce being present as Ce^{4+} . Reproduced from Liebske C, Corgne A, Frost DJ, Rubie DC, and Wood BJ (2005) Compositional effects on element partitioning between Mg-silicate perovskite and silicate melts. *Contributions to Mineralogy and Petrology* 149: 113–128.

2.04.2.2.2 Effects of Al content on large trivalent and tetravalent cations

As mentioned earlier, Al and Fe are two elements that are likely to influence the MgPv-melt partitioning of trace elements. Liebske et al. (2005) investigated the effects of Al and Fe contents of MgPv on trace element partitioning at similar conditions of pressure and temperature. They found, however, no evidence of a significant effect of bulk Fe content on trace element partitioning, even with large amounts of FeO (up to 35 wt.%). Increasing Al content of Mg-perovskite was also found not to influence partitioning of divalent cations. Partitioning of large trivalent and tetravalent cations is, however, sensitive to the Al content of perovskite, as shown in Figures 6 and 7. Both figures show that partition coefficients for trivalent and tetravalent cations entering the A-site increase with increasing MgPv Al content. The effect is the largest for light REE, D_{La} increasing by an order of magnitude as Al_2O_3 increases from ~0 to 6.5 wt.%. Ti, Zr, and Hf are incompatible in Al-free MgPv but become compatible as Al is added in the crystal structure.

Substitution of trivalent and tetravalent cations into the large A-site requires charge compensation. Two main mechanisms have been proposed: (1) Al-coupled substitution into the B-site and (2) the creation of Mg vacancies (e.g., Corgne

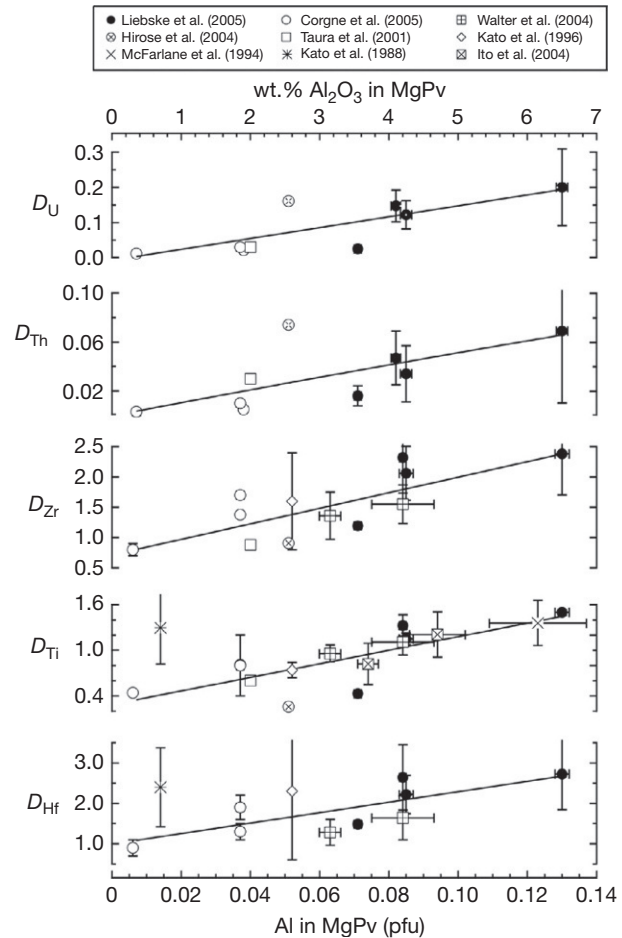


Figure 7 MgPv-melt partition coefficients for tetravalent elements as a function of Al per formula unit in MgPv (normalized to two cations pfu).

et al., 2003). The correlation between trivalent and tetravalent cation partition coefficients and MgPv Al content seems to support the first mechanism although incorporation of Al may also influence the energetics of Mg-vacancy formation. Heterovalent substitution in the large site of silicate perovskites is discussed further in Section 2.04.2.3.

2.04.2.2.3 Other potential effects

Apart from crystal composition, additional influences on partitioning behavior include pressure, temperature, and melt composition. Due to experimental limitations, MgPv–melt partition coefficients have been generated for a very restricted range of pressure and temperature conditions. This means that it is currently impossible to separate the effects of the two intensive variables on partitioning. As for majoritic garnet, the effect of melt composition on partitioning is unknown. Although computational simulations (Corgne et al., 2003) indicate that melt composition is a significant factor, variation of measured partition coefficients can, to date, be explained without calling for a ‘melt contribution’ (e.g., Liebske et al., 2005).

2.04.2.3 Calcium Silicate Perovskite

2.04.2.3.1 Crystal chemistry

Figure 8 shows crystal–melt partition coefficients for trace elements entering the large site of CaSiO_3 perovskite (CaPv) at 25 GPa and 2300 °C (Corgne et al., 2005). In this case, CaPv was crystallized from a nonperidotitic calcium-enriched composition and contained 1.6 wt.% Al_2O_3 . As can be seen, the partitioning patterns of elements of different charge broadly fit the lattice strain model of Blundy and Wood (1994). As found for upper-mantle silicates (e.g., van Westrenen et al., 2000), majoritic garnet (Corgne and Wood, 2004; see Figure 3), and in agreement with recent atomistic simulations (Corgne et al.,

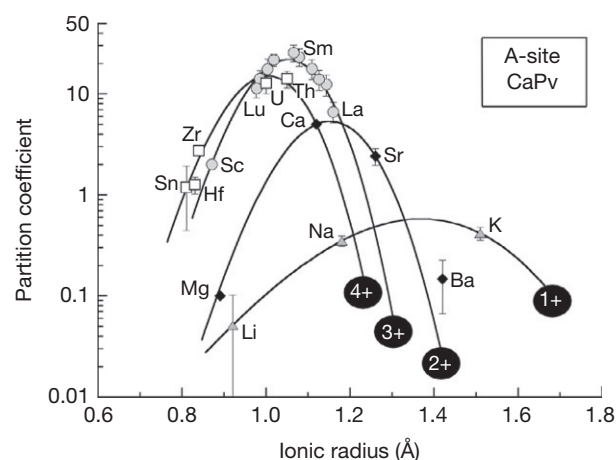


Figure 8 Partition coefficients for elements entering the A-site of calcium silicate perovskite (CaPv) as a function of ionic radius. Parabolas are fits of eqn [1] to experimental data from Corgne et al. (2005). In comparison to MgPv (Figure 5) at identical conditions of pressure and temperature (~25 GPa, ~2300 °C), CaPv accepts more readily elements normally regarded as incompatible. Ionic radii are values for an eightfold coordinated site taken from Shannon (1976), as no consistent set of 12-fold coordinated radii exists.

2003), r_o decreases and E_s generally increases with increasing charge of the cation incorporated at the large site of both $(\text{Mg,Fe})\text{SiO}_3$ and CaSiO_3 perovskites. Comparison between the partition coefficients measured for MgPv (Figure 5) and those measured for CaPv (Figure 8) shows that the calcic phase much more readily accepts elements normally regarded as strongly incompatible. D_o^{3+} and D_o^{4+} for the large A-site are roughly one order of magnitude lower for MgPv than for CaPv. Furthermore, because of the differences in r_o^{3+} and r_o^{4+} between the A-site of MgPv and the A-site of CaPv, crystallization of CaPv fractionates the ratios of many RLEs (e.g., Sc/Sm, Lu/Hf, and U/Th) in the opposite sense to crystallization of MgPv. When coupled with the effect of ionic size, the differences between the two perovskites mean that, despite being volumetrically subordinate to MgPv, CaPv contains more than 90% of the heat-producing elements K, U, and Th in the lower mantle, together with most of the light REEs, Sr and Ba. The relative ease of entry of highly charged ions into both phases is unusual, however, and prompted experimental and theoretical investigations of the mechanisms by which charge balancing occurs in these phases (Corgne and Wood, 2005).

2.04.2.3.2 Substitution mechanisms in calcium silicate perovskite

Clear resolution of substitution mechanisms for $(\text{Mg,Fe})\text{SiO}_3$ and CaSiO_3 perovskites are difficult tasks, requiring, in principle, large numbers of experiments at high pressures and temperatures. There are, however, potential shortcuts provided by calculations of the energetics of the different potential mechanisms (Corgne et al., 2003) and, experimentally, by use of the low-pressure analog of CaSiO_3 and CaTiO_3 . The patterns of partitioning of trace elements into CaTiO_3 and CaSiO_3 perovskites are virtually identical, as shown in Figure 9 (Corgne and Wood, 2002). Furthermore, like CaSiO_3 perovskite, CaTiO_3 adopts the $Pm3m$ cubic structure above ~1550 K, and mechanisms of charge compensation might reasonably be expected to be the same in the two perovskites. Because large crystals of CaTiO_3 perovskite can be easily obtained at 1 atm, work on CaTiO_3 circumvents the experimental and analytical

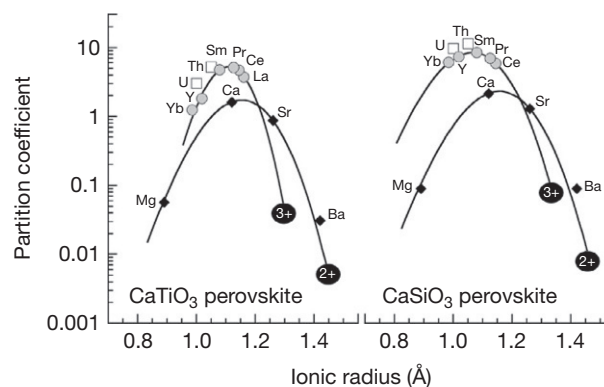


Figure 9 Comparison of partitioning behavior for 2+, 3+, and 4+ cations entering the A-site of CaSiO_3 and CaTiO_3 perovskites. Reproduced from Corgne A and Wood BJ (2002) CaSiO_3 and CaTiO_3 perovskite–melt partitioning of trace elements: Implications for gross mantle differentiation. *Geophysical Research Letters* 29, <http://dx.doi.org/10.1029/2001GL014398>.

challenges related to the generation of large numbers of CaSiO_3 perovskite–melt partition coefficients.

Determining the concentration limits of Henry's law behavior in CaTiO_3 perovskite enables identification of the most likely substitution mechanisms for Ca by 3+ and 4+ cations such as Pr^{3+} and Th^{4+} . In the absence of Al^{3+} to substitute for Ti^{4+} , the energetically favorable mechanism for incorporation of Pr^{3+} is through the generation of calcium vacancies V_{Ca}'' (Corgne et al., 2003). Corgne and Wood (2005) showed that if this is the only substitution mechanism, D_{Pr} should be a linear function of the reciprocal of the square root of vacancy concentration $[V_{\text{Ca}}'']$, while D_{Th} should be a linear function of the reciprocal of $[V_{\text{Ca}}'']$. Calcium vacancies can be formed in two ways. There are those vacancies generated as part of the heterovalent substitution (V_s), which depend linearly on the amount of trace ion added to the crystal, and those intrinsically present in the pure crystal (V_i). If V_i dominate, then $[V_{\text{Ca}}'']$ is constant, and D_{Pr} and D_{Th} should be independent of the concentrations of Pr and Th in calcium perovskite, that is, Henry's law behavior. If, on the other hand, V_s dominate over V_i , then vacancy concentration and hence D_{Pr} and D_{Th} must depend on the concentrations of Pr and Th in the perovskite (noted $[\text{Pr}_{\text{Ca}}^{\bullet}]$ and $[\text{Th}_{\text{Ca}}^{\bullet\bullet}]$ in the succeeding text). Corgne and Wood (2005) found that the latter case leads to

$$D_{\text{Pr}}^{\text{CaPv-Liq}} \approx \text{constant} \cdot [\text{Pr}_{\text{Ca}}^{\bullet}]^{-1/2} \quad [2]$$

$$D_{\text{Th}}^{\text{CaPv-Liq}} \approx \text{constant} \cdot [\text{Th}_{\text{Ca}}^{\bullet\bullet}]^{-1} \quad [3]$$

Figure 10(a) shows a plot of D_{Pr} versus the inverse of the square root of $[\text{Pr}_{\text{Ca}}^{\bullet}]$ for one specific composition (CAST) studied by Corgne and Wood (2005). At high Pr content in perovskite, D_{Pr} is approximately a linear function of the inverse of the square root of $[\text{Pr}_{\text{Ca}}^{\bullet}]$. This agrees with a mechanism of substitution via Ca-vacancy formation with a predominance of V_s over V_i . At $[\text{Pr}_{\text{Ca}}^{\bullet}]$ lower than ~ 1000 ppm, D_{Pr} is constant and independent of $[\text{Pr}_{\text{Ca}}^{\bullet}]$ and Henry's law is obeyed. At concentrations below ~ 1000 ppm Pr in perovskite, therefore, it appears that V_i dominate over V_s . Similar conclusions can be drawn for Th from Figure 10(b). At high Th contents, D_{Th} is approximately a linear function of the inverse of $[\text{Th}_{\text{Ca}}^{\bullet\bullet}]$ ($V_s \gg V_i$), while at Th contents lower than ~ 1000 ppm, D_{Th} is constant ($V_i \gg V_s$).

If Al is added to the system, then it is possible, in addition to vacancy formation, to charge-compensate the insertion of Pr^{3+} or Th^{4+} for Ca^{2+} by coupled replacement of Al^{3+} for Ti^{4+} . Corgne and Wood (2005) showed, however, that the dependencies of partition coefficients on Pr and Th concentrations are the same in both Al-bearing and Al-free compositions. Furthermore, using similar arguments to those outlined earlier, they were able to show that the compositional dependence of partitioning is consistent with calcium vacancies being the dominant mechanism of charge compensation in Al-bearing and Al-free bulk compositions.

2.04.2.3.3 Effects of melt composition

Melt composition is known to be an important factor controlling the partitioning of trace elements between silicates and melts. In this case, it has been observed that partition coefficients for 3+ and 4+ ions into perovskite depend strongly on the CaO content of the coexisting melt (Corgne and Wood, 2005; Corgne et al., 2005; Hirose et al., 2004; Walter et al., 2004). Considering formation of cation vacancies as the dominant substitution mechanism for REE and Th^{4+} into the Ca-site of perovskite and assuming that the activity of CaO in the melt varies as an approximately linear function of the CaO concentration, $[\text{CaO}]$, Corgne and Wood (2005) predicted the following dependencies in the Henry's law region:

$$D_{\text{Pr}}^{\text{CaPv-Liq}} \approx \alpha \cdot [\text{CaO}_{\text{Liq}}]^{-3/2} \quad [4]$$

$$D_{\text{Th}}^{\text{CaPv-Liq}} \approx \beta \cdot [\text{CaO}_{\text{Liq}}]^{-2} \quad [5]$$

where α and β are constants.

As can be seen from Figure 11, both D_{Pr} and D_{Th} decrease with increasing CaO content of the melt and fit well to the models represented by eqns [4] and [5]. Since these equations are based on the cation vacancy mechanism of charge compensation, the fits further support this being the predominant substitution mechanism. They also indicate that charge compensation cannot be via oxygen interstitial incorporation. In the latter case, a dependence of partition coefficient on $[\text{CaO}]^{-1}$ should be observed. Such a compositional dependence is much weaker than that observed in the data of Figure 11 indicating that this mechanism of charge compensation is not important.

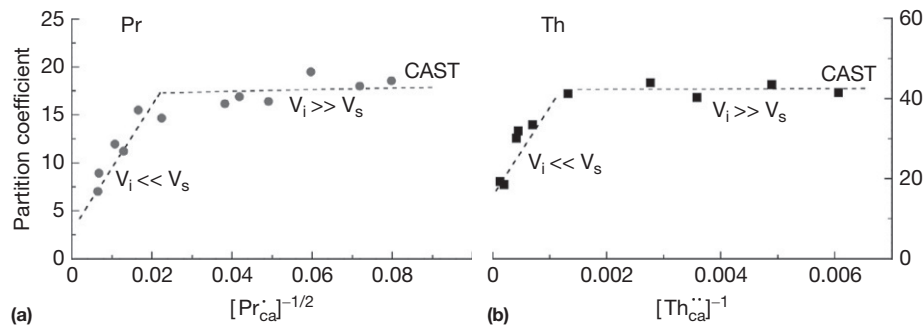


Figure 10 Plots of (a) D_{Pr} versus $[\text{Pr}_{\text{Ca}}^{\bullet}]^{-1/2}$ and (b) D_{Th} versus $[\text{Th}_{\text{Ca}}^{\bullet\bullet}]^{-1}$ showing evidence for Ca-vacancy formation as the likely charge-balance mechanism for the substitution of Pr and Th at the Ca-site. At low perovskite contents of Pr and Th or high $[\text{Pr}_{\text{Ca}}^{\bullet}]^{-1/2}$ and $[\text{Th}_{\text{Ca}}^{\bullet\bullet}]^{-1}$, intrinsic Ca-vacancies (V_i) dominate Ca-vacancies formed as part of the substitution (V_s). D_{Pr} and D_{Th} are maximum until V_i content is not large enough to account for higher contents of Pr and Th. When V_s dominates, D_{Pr} and D_{Th} are a linear function of $[\text{Pr}_{\text{Ca}}^{\bullet}]^{-1/2}$ and $[\text{Th}_{\text{Ca}}^{\bullet\bullet}]^{-1}$. Data are from Corgne and Wood (2005) for a bulk composition chosen in the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-TiO}_2$ system (CAST).

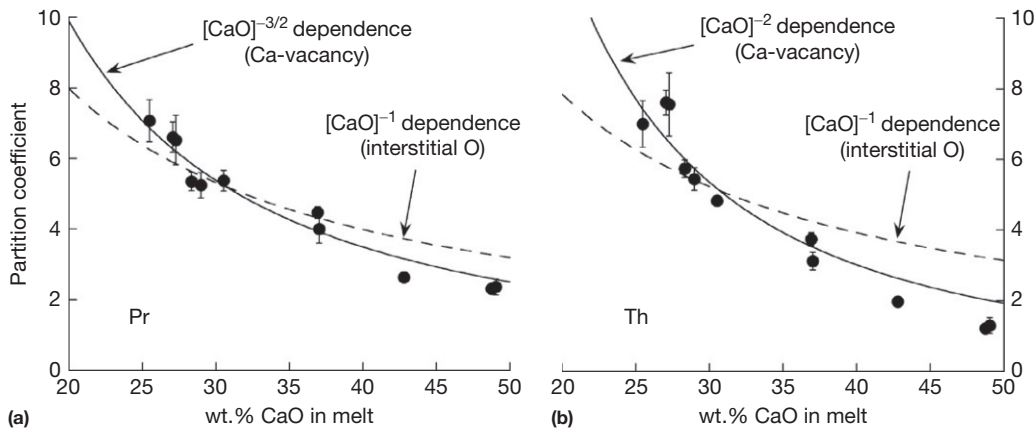


Figure 11 Variations of (a) D_{Pr} and (b) D_{Th} as a function of CaO content of the melt. The good agreement between data and models represented by eqns [4] and [5] indicates that Ca-vacancy formation rather than oxygen interstitial incorporation is the likely charge-balance mechanism for the substitution of 3+ and 4+ cations in the A-site of CaPv. Reproduced from Corgne A and Wood BJ (2005) Trace element partitioning and substitution mechanisms in calcium perovskites. *Contributions to Mineralogy and Petrology* 149: 85–97.

2.04.2.3.4 Comparison between CaTiO_3 and CaSiO_3 perovskites

Figure 9 shows that the forms and heights of the partitioning parabolas for CaTiO_3 and CaSiO_3 perovskites are very similar, which is the reason why the former was used as an analog to investigate the behavior of the latter, lower-mantle phase. When data for the two phases are inspected more closely, however, the similarities between them become even more striking. In Figure 12, partition coefficients for 2+, 3+ (both as D_o , the peak of the partitioning parabola), and 4+ (Th) ions entering the Ca-sites of the two perovskites are plotted as functions of the CaO content of the coexisting liquids. As can be seen, the data for each charge form one continuous line as a function of melt composition, 'independent of whether the solid is CaSiO_3 or CaTiO_3 .' Thus, on the right-hand side of the diagram are data collected at 1 atm and about 1400 °C on CaTiO_3 perovskite, while on the left are results obtained for CaSiO_3 at around 25 GPa and 2200–2300 °C. Despite the differences in composition and pressure and temperature conditions, the trace element partitioning behavior is identical. All that seems to be important is that these elements are entering the Ca-sites in perovskites with the same crystal structure. The result demonstrates that low-pressure experiments on CaTiO_3 perovskite are near-perfect analogs of experiments on CaSiO_3 perovskite at high pressure. Note that the dependence of D_o^{2+} on the inverse of $[\text{CaO}]_{\text{Liq}}$ reflects the fixed CaO content of perovskite and does not require defect substitution (Corgne and Wood, 2005).

One important implication of the partitioning data is that, despite being a volumetrically minor phase, CaSiO_3 perovskite is the major host for the heat-producing elements Th and U in the deep Earth, as well as being the principal reservoir for the REEs (Corgne et al., 2005). Observed solid-liquid partition coefficients for Th are in the range 30–60 in CaSiO_3 crystallizing from Ca-rich compositions, but extrapolation of the defect model to peridotitic compositions (3–3.5 wt.% CaO) suggests that D_{Th} and D_U should be closer to 400 in the mantle (Figure 12). Thus, crystallization of as little as 0.25 vol. % of CaSiO_3 perovskite from an early earth magma ocean could, if it had remained isolated in the lower mantle, contribute substantially to current mantle heat production.

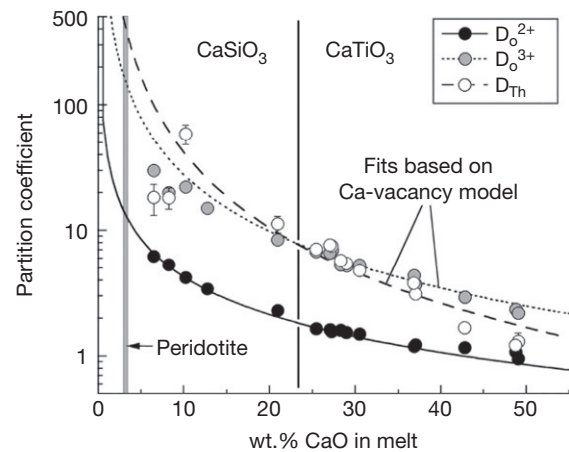


Figure 12 Figure showing D_o^{2+} , D_o^{3+} , and D_{Th} as a function of CaO content in the melt for both CaSiO_3 and CaTiO_3 perovskites. Data for CaTiO_3 perovskite are from Corgne and Wood (2005). Data for CaSiO_3 perovskite are from the experiments S2738 (Corgne and Wood, 2002); LO#50, LO#111, and LO#113 (Hirose et al., 2004); H2020b (Corgne et al., 2005); and 266 (Kato et al., 1988). Interestingly, D_o^{3+} and D_{Th} for CaSiO_3 perovskite follow the trends derived from the study of the low-pressure analog.

2.04.2.4 Trace Elements in Other Mantle Minerals

Trace element partitioning data for other minerals of the transition zone and lower mantle are limited. As shown briefly in the succeeding text, the effects of these minerals on trace element distribution during mantle differentiation are likely to be minor given that most of geochemically important trace elements are expected to be highly incompatible in these phases, except perhaps for postperovskite.

2.04.2.4.1 Wadsleyite and ringwoodite

Crystal-melt partition coefficients for wadsleyite (Wad) have been determined by McFarlane (1994) for Cr, Sc, Ni, and Mn. $D^{\text{Wad-Liq}}$ for these elements are, respectively, about 0.8, 0.1, 2, and 1. Considering the value obtained for D_{Sc} , one should expect D values lower than 0.1 for larger trivalent cations

such as REE and Y. Wadsleyite–olivine partition coefficients for minor elements were also determined by Gudfinnsson and Wood (1998). The results indicate that crystal–melt partition coefficients for elements entering the large Mg-site are likely to have similar magnitude for both minerals. Therefore, given the results obtained for olivine (e.g., McDade et al., 2003), 4+ and 5+ cations such as U, Th, Ta, and Nb are expected to be highly incompatible in wadsleyite. These predictions are confirmed by partitioning data obtained for hydrous compositions at 14–16 GPa and 1400–1600 °C (Mibe et al., 2006; Wood, unpublished data). In these systems, $D^{\text{Wad-Liq}}$ values for REE are <0.002 (obtained for Lu), and D_{Sc} is ~ 0.04 , a value similar to the one derived for the optimum partition coefficient D_{o}^{3+} for the Mg-site. Moreover, U, Th, Hf, Zr, Ta, Nb, Rb, Sr, and Pb are found to be highly incompatible too.

Because of structural similarities between ringwoodite and the lower-pressure polymorphs olivine and wadsleyite, it is probable that REE, U, and Th are highly incompatible in this phase. Partitioning of minor elements between wadsleyite and ringwoodite (Gudfinnsson and Wood, unpublished data) indicates that ringwoodite does not exhibit strong trace element preferences and is relatively ‘sterile’ with respect to incompatible elements. Note, however, that despite their apparent geochemical ‘inaction,’ ringwoodite and wadsleyite may play an important role during melting of peridotite given that these minerals have significant water-storage capacity (see Section 2.04.4).

2.04.2.4.2 Ferropericlase

(Mg, Fe)O, ferropericlase, is an important constituent of the lower mantle (Figure 2), comprising about 16% by mass of peridotitic compositions under lower-mantle conditions (Wood, 2000). It crystallizes in the cubic $Fm\bar{3}m$ structure with one octahedral site (A) occupied nominally by divalent cations Mg and Fe. Walter et al. (2004) determined ferropericlase–melt partition coefficients for a series of trace elements. Despite large measurement uncertainties, it can be shown that most trace elements, with the exceptions of Cr, Fe, Mg, and Ni, are incompatible in ferropericlase. In particular, REE have D values below 0.1. U and Th were not measured but are expected to be highly incompatible based on the results obtained for other 4+ cations (Si, Ti, Zr, and Hf). Furthermore, Al, Ba, Na, and Mn are moderately incompatible ($D \sim 0.3$ – 0.8) and Nb is highly incompatible ($D \sim 0.002$).

2.04.2.4.3 Postperovskite

A new polymorph of MgSiO_3 with a structure more stable than the $Pbnm$ perovskite phase has recently been identified at pressures and temperatures corresponding to the lowermost part of the Earth's mantle by both experimental and theoretical techniques (Murakami et al., 2004; Oganov and Ono, 2004). The MgSiO_3 -rich postperovskite (MgPP) structure belongs to the space group $Cmcm$ and consists of layers of SiO_6 octahedra alternating with layers of Mg atoms in approximate eightfold coordination. Current experimental data indicate that MgPP is unlikely to be stable in the mantle at liquidus temperatures (~ 4000 K) (e.g., Fiquet et al., 2010; Shim, 2008), and hence, this phase would not have been involved in crystal differentiation of an early magma ocean. Nevertheless, it is important that future experiments are aimed at determining MgPP–MgPv partitioning of trace elements to constrain chemical exchange

that may have taken place in the lowermost mantle once MgPP became a stable phase.

Performing MgPP–MgPv partitioning experiments is currently challenging due to the extreme conditions of pressure and temperature that are required and to the difficulty of analyzing very small crystals. In the absence of experimental data, it is impossible to know how the differences in structure between MgPv and MgPP influence trace element partitioning. One way forward would be to combine experimentation in the laser-heated diamond anvil cell with nanoscale analytical techniques (Badro et al., 2007). Such an approach would also be a useful way of determining the effects of temperature and pressure on CaPv–melt and MgPv–melt partitioning of trace elements. Current data on these phases are limited to conditions of the uppermost lower mantle. An alternative approach would be to perform computer simulations similar to those of Corgne et al. (2003) and compare the energies associated with the incorporation of trace elements in both MgPP and MgPv. Iitaka et al. (2004) had calculated that the average Si–O and Mg–O distances in MgPP are, respectively, $\sim 1\%$ longer and $\sim 1\%$ shorter than in MgPv of pure MgSiO_3 composition. This indicates that optimum radii r_o for the Si- and Mg-sites are, respectively, larger and smaller in MgPP than in MgPv. Therefore, elements larger than Si and smaller than Mg should be incorporated more easily in MgPP than in MgPv. On the other hand, elements larger than Mg (e.g., REE, K, U, and Th) should have partition coefficients higher in MgPv than in MgPP, that is, these elements should be highly incompatible in MgPP. Recent experimental results of Sinmyo et al. (2011) confirm significant differences between MgPv and MgPP in terms of partitioning behavior. The perovskite phase was found to have strong preferences for both Fe^{2+} and Fe^{3+} relative to post-perovskite. The combined effect means that during the MgPv–MgPP transition, Fe^{3+} recombines with metallic Fe to form Fe^{2+} , and the Fe^{2+} produced is partitioned preferentially into the coexisting ferropericlase (Mg,Fe)O. The results indicate that the fraction of Fe^{3+} in MgPP is much less than that in coexisting MgPv, contradicting the predictions of Oganov and Ono (2004). It is clear that MgPv and MgPP have quite different abilities to accommodate vacancies and other defects and that future experimental and theoretical work will be needed to more fully understand the trace element partitioning behavior of postperovskite. As discussed in the preceding text, however, this phase should not generally be stable at the mantle liquidus.

2.04.3 Implications for Planetary Differentiation and Trace Element Distribution in the Deep Mantle

2.04.3.1 A Primitive Majoritic or Perovskitic Reservoir?

Melting experiments on peridotitic compositions have shown that majoritic garnet is the liquidus phase at depths of the transition zone (e.g., Trønnes and Frost, 2002). The liquidus phase is ferropericlase between about 24 and 30 GPa and magnesium silicate perovskite above 30 GPa, followed closely by ferropericlase in lower temperatures and calcium silicate perovskite (Fiquet et al., 2010; Ito et al., 2004; Trønnes and Frost, 2002). Global melting and subsequent fractionation and gravitational settling of majoritic garnet or silicate perovskites in a magma ocean has been proposed as a mechanism for

forming a PUM with high Mg/Si and Ca/Al ratios (e.g., Herzberg et al., 1988; Ohtani et al., 1986; Ringwood, 1979). The difficulty with this hypothesis is that it is required to have occurred without significantly changing the ratios of RLEs to one another in the residual melt, that is, in the PUM (Figure 1). Crystal-melt partition coefficients for majoritic garnet and silicate perovskites obtained in high-pressure experiments enable us to calculate the maximum volume of any majoritic and/or surviving perovskitic reservoir in the lower mantle using the constraint that RLE ratios in the PUM are chondritic. Attempts were made to perform this calculation some time ago with limited data and dramatically different conclusions (e.g., Agee and Walker, 1988; Kato et al., 1988). Recent results however (Corgne and Wood, 2004; Corgne et al., 2005; Liebske et al., 2005; Walter et al., 2004) point to the allowable extent of a deep majoritic or perovskitic reservoir being small.

Figure 13(a) shows the variations of RLE ratios of the residual melt (PUM) as a function of majoritic garnet fractionation as calculated by Corgne and Wood (2004). Due to low D

values, Sm and Nd are not fractionated one from another significantly during crystallization of majorite, which means that the Sm/Nd ratio remains in the PUM range. In contrast, the Pr/Sc, Gd/Yb, Lu/Hf, and Lu/La ratios are all driven outside the PUM range after <25% of majoritic garnet fractionation. The strongest constraint on majorite fractionation is given by the Pr/Sc ratio, for which the maximum allowable extent of majoritic garnet fractionation is 14%. In other words, <14% fractionation of majoritic garnet would not be detected in the composition of PUM, assuming that the PUM composition of McDonough and Sun (1995) is correct. Given chondritic ratios of RLEs in PUM, no more than 14% majoritic garnet fractionation may have survived from an early magma ocean. This value compares with an even smaller maximum majorite fractionation of 4% estimated by Walter et al. (2004) using similar D values but different elemental ratios in the PUM (Ca/Al, Al/Mg, Al/Sc, and Al/Yb being the most constraining). Furthermore, isotopic ratios in modern volcanic rocks effectively preclude any significant fractionation of majoritic garnet, since such fractionation would lower considerably both $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ ratios of the residual peridotitic liquid (PUM) and drive its geochemical signature away from that of the observed mantle array (e.g., Blichert-Toft and Albarède, 1997; Corgne and Wood, 2004).

Figure 13(b) shows the variations of RLE ratios of the residual melt (PUM) as a function of perovskite fractionation as calculated by Corgne et al. (2005). The ratios Sr/Sc and Sm/Ba, which give the strongest constraints, are used to place bounds on the volume of the hypothetical perovskitic reservoir. For MgPv crystallization alone, Sr/Sc is driven outside the chondritic range after only 6.5% of crystallization. The addition of CaPv to the crystallizing assemblage increases the allowed amount of fractionation to, for instance, 9% when the ratio of MgPv/CaPv is 80:20. Taking account of both Sr/Sc and Sm/Ba ratios, it appears that the allowable extent of perovskite fractionation is a maximum for a mixture containing 5–10% CaPv. Under these circumstances, ~8% fractionation would not be detected in the composition of the PUM. Similar conclusions were arrived at by Liebske et al. (2005) and Walter et al. (2004). Following a similar approach to that outlined in the preceding text and incorporating Nd and Hf isotopic constraints, Walter et al. (2004) concluded that 10–15% (but no more) fractionation of a lower-mantle assemblage consisting of 93:3:4 MgPv/CaPv/FP could yield the current upper mantle as residuum.

The results in the preceding text mean that the PUM depletion relative to CI chondrite in Si (Figure 1) cannot be due to majorite or perovskite fractionation since ~60% crystallization would be required. The silicate Earth is depleted in Si either due to its volatility during accretion (e.g., Ringwood, 1979) or due to its incorporation in the core (Allègre et al., 1995; Tuff et al., 2011; Wade and Wood, 2005). The putative perovskitic reservoir would be enriched in U and Th relative to PUM, if the CaPv proportion were greater than ~7%, assuming $D^{\text{CaPv-Liq}}$ values for U and Th of ~15 as determined experimentally by Corgne et al. (2005). Note that if $D^{\text{CaPv-Liq}}$ values for U and Th for a peridotite composition are ~400 as suggested by extrapolation of the Corgne and Wood (2005) data, a small fraction of CaPv (>0.25%) isolated from the residual melt would be sufficient to produce a heat-producing reservoir in the deep

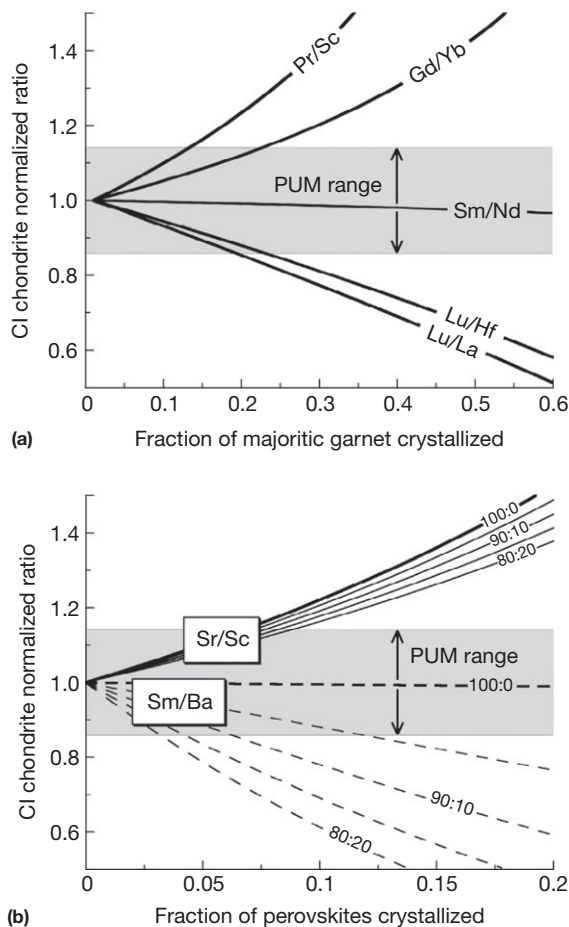


Figure 13 Variation of normalized refractory lithophile element (RLE) ratios in the residual melt as a function of fractionation of (a) majoritic garnet and (b) perovskites during a magma ocean stage. Numbers on lines in (b) refer to proportions of MgPv and CaPv perovskites. Gray boxes show range of ratios in the PUM assuming that contents of RLEs are known within 15% (e.g., McDonough and Sun, 1995). Partition coefficients are taken from Corgne and Wood (2004) and Corgne et al. (2005).

mantle. Recent measurements also suggest that the putative perovskitic reservoir could have concentrated a significant amount of Ar due to its relatively high solubility in MgPv (Shcheka and Keppler, 2012). If the perovskitic reservoir contained enough CaPv, it would also have higher Lu/Hf, U/Pb, Sr/Rb, and Sm/Nd ratios than the PUM and hence have the major geochemical characteristics of the HIMU (high $^{238}\text{U}/^{204}\text{Pb}$) component of OIBs. Since, however, the latter can be interpreted as recycled MORBs (Hofmann and White, 1982), it would be extremely difficult to distinguish a small perovskitic reservoir in the lower mantle on the basis of its isotopic properties. Furthermore, since majoritic garnet, MgPv, and CaPv all prefer Sm to Nd, the putative majoritic or perovskitic layer can clearly not be the low Sm/Nd reservoir required to balance terrestrial samples with superchondritic $^{142}\text{Nd}/^{144}\text{Nd}$ with a chondritic silicate Earth (Boyett and Carlson, 2005).

2.04.3.2 Deep Segregation of Dense Melts?

Since crystallization of a magma ocean in early Earth history was initially thought to have proceeded from the bottom-up (e.g., Solomatov, 2000), residual melts were generally regarded as migrating upward. Caro et al. (2005), for example, proposed that the Nd and Hf isotopic signatures of the Hadean depleted mantle may have been acquired after formation of a protocrust produced by melt extracted from a crystallizing magma ocean at upper-mantle pressures. An alternative suggestion is that melts at high pressures are denser than the surrounding mantle minerals and could remain isolated at great depths (e.g., Suzuki and Ohtani, 2003). Olivine flotation might also have occurred within a limited depth interval of 400–450 km in a terrestrial magma ocean (Suzuki and Ohtani, 2003). The impact of olivine fractionation on trace element patterns would be small, however, given the low crystal–melt partition coefficients obtained for olivine and its high-pressure polymorphs. Of more interest is the possibility of dense melts segregating downward from majorite and silicate perovskites. Recent molecular dynamics simulations in the MgSiO_3 system (Stixrude and Karki, 2005; Stixrude et al., 2009) and shock-wave experiments in the MgSiO_3 , Mg_2SiO_4 , and Fe_2SiO_4 systems (Mosenfelder et al., 2009; Thomas et al., 2012) suggest that the density contrast between melt and crystals decreases with increasing pressure, such that a density crossover near the base of the mantle may take place. In the present-day Earth, the existence of dense melts provides a possible explanation for the ultralow-velocity zone at the base of the mantle (e.g., Andrault et al., 2011; Fiquet et al., 2010; Stixrude et al., 2009; Thomas et al., 2012; Williams and Garnero, 1996). Composition is, however, a key variable and other experimental results suggest that, in a peridotite composition (as opposed pure to MgSiO_3), melts may be less dense than mantle minerals over the entire pressure range of the lower mantle (Agee, 1998; Thomas et al., 2012).

Given the possibility of a density crossover, Hofmann et al. (2005) suggested that downward migration of dense melts formed in the deep mantle in equilibrium with CaPv could have created a deep ‘missing’ reservoir unradiogenic in Pb (with a U/Pb ratio lower than that of PUM) as required to balance the Pb composition of the bulk MORB- and

OIB-source reservoirs. This reservoir would have a complementary signature to the putative majoritic or perovskitic reservoir discussed in Section 2.04.3.1. Thus, it could also be the missing subchondritic $^{142}\text{Nd}/^{144}\text{Nd}$ reservoir. Alternatively, Boyett and Carlson (2005) proposed that the missing reservoir could be an early KREEP-like liquid formed at shallow depths but subsequently isolated in the deepest mantle due to its relatively high density. Finally, Lee et al. (2010) suggested that the ‘upside-down differentiation’ proposed by Hofmann et al. (2005) could have generated dense melts in the deep PUM that would have subsequently migrated downward in the lowermost mantle to form a reservoir with ‘primordial’ trace element and noble gas isotopic signatures as observed in the ‘FOZO’ geochemical component.

Labrosse et al. (2007) presented a model for the generation of a deep geochemical reservoir following crystallization of a basal magma ocean. In this scenario, crystallization of the magma ocean would have begun at mid-mantle depths, rather than at its base. As crystallization proceeded, deep melts would have become gradually more enriched in Fe and subsequently generated a solidified reservoir sufficiently dense to remain isolated from the convecting mantle. Present-day ultralow-velocity zones on top of the core–mantle boundary would represent partially molten remnants of the basalt magma ocean. The putative reservoir would be an ideal candidate for hosting a variety of incompatible species such as heat-producing elements and noble gases and could balance the ^{142}Nd signature of the bulk silicate Earth (Coltice et al., 2011; Labrosse et al., 2007). The viability of a deep-mantle reservoir with subchondritic $^{142}\text{Nd}/^{144}\text{Nd}$ has remained controversial, however. Caro (2011) has, for example, pointed out that the ‘hidden’ reservoir must have formed sufficiently early – within 20 Ma after formation of the solar system – to explain the excess of ^{142}Nd observed in the ‘accessible’ Earth. This poses chronological issues as the reservoir must have been able to survive the ongoing process of core formation and the late Moon-forming giant impact. Furthermore, the lack of contributions to surface volcanism would indicate a complete isolation of the putative reservoir (e.g., Boyett and Carlson, 2005; Caro et al., 2008), although recent ^{182}W isotopic data hint at a possible contribution of an old distinct reservoir in the source of 2.8 Ga old komatiites (Touboul et al., 2012). Rather than calling upon a deep complementary reservoir, Caro and coworkers have suggested that the Earth more likely accreted from materials with a Sm/Nd ratio about 5% above the chondritic value (Caro, 2011; Caro et al., 2008), possibly as a consequence of collisional erosion during planetary accretion (Campbell and O'Neill, 2012; Korenaga, 2009; O'Neill and Palme, 2008).

2.04.3.3 Recycled Lithosphere in the Deep Mantle?

As discussed in the preceding text, the HIMU component of OIBs can be interpreted as due to mixing of recycled oceanic crust into their source regions. Such a reservoir, rather than originating at the end of accretion, may have formed through geologic time by the accumulation of recycled lithosphere in the lower mantle (e.g., Albarède and van der Hilst, 2002; Hofmann and White, 1982). Experimental support for this idea comes from data indicating that subducted MORB crust

is denser than the surrounding mantle over its entire pressure range (Hirose et al., 2005). Transformation of the original low-pressure minerals to an assemblage containing lower-mantle minerals, including MgPv, CaPv, stishovite, CaFe_2O_4 -type Al-phase, and possibly MgPP, without loss of trace elements could lead to formation of a long-lived geochemical reservoir enriched in elements normally regarded as incompatible (K, U, Th, REE, etc.). Various versions of this model have been proposed including storage of subducted oceanic crust in the lowermost lower mantle (Hanyu et al., 2011; Tolstikhin et al., 2006) and admixing of old subducted continental crust (Komabayashi et al., 2009), but the important point of this model for the HIMU component is that it relies on a process, subduction, which is well known.

2.04.4 Water in the Deep Mantle

In this section, we review the present state of our understanding of water distribution in the transition zone and lower mantle. We do not present constraints from electrical conductivity since geophysical measurements still lack the required resolution to infer water contents in the mantle (Karato, 2011). Instead, we present a summary of water-solubility measurements in deep-mantle minerals together with theoretical considerations regarding the mechanisms of water incorporation in the crystal lattice of these minerals. The presence of minor components and volatile species is expected to broaden seismic discontinuities (e.g., Gudfinnsson and Wood, 1998; Wood, 1995). Using recent high-pressure experimental data, we present an updated model that constrains water contents in the transition zone and lower mantle based on observed widths of seismic discontinuities. We discuss the implications that such water contents have for mantle dynamics and differentiation processes.

2.04.4.1 Water Solubility in Minerals from the Transition Zone

Following the predictions by Smyth (1987, 1994) that wadsleyite could store a large amount of water, Kohlstedt et al. (1996) determined the water-storage capacity of olivine, wadsleyite, and ringwoodite as a function of pressure at 1100 °C using Fourier transform infrared (FTIR) spectroscopy and the spectroscopic calibration of Paterson (1982). The latter has been shown more recently to underestimate the water concentration in olivine by a factor of ~ 3 – 3.5 , however (Bell et al., 2003; Koga et al., 2003). After applying the newer correction, the experiments of Kohlstedt et al. (1996) indicate that olivine can store up to ~ 5000 ppm water (by weight) at pressures close to the 410 km discontinuity, in agreement with the experimental results of Chen et al. (2002). Wadsleyite–olivine partition coefficients ($D^{\text{Wad-Ol}}$) suggest that the high-pressure polymorph has larger water-storage capacity. Applying the correction, the FTIR results of Young et al. (1993) imply that $D^{\text{Wad-Ol}}$ is between 10 and 30, while those of Kohlstedt et al. (1996) imply that $D^{\text{Wad-Ol}}$ is ~ 6 . More recent SIMS measurements favor the latter estimate. Chen et al. (2002) reported $D^{\text{Wad-Ol}}$ of ~ 5 in $(\text{Mg}_{0.91}\text{Fe}_{0.09})_2\text{SiO}_4$ synthesized at ~ 13 GPa and 1200 °C, while Deon et al. (2011) calculated a partition

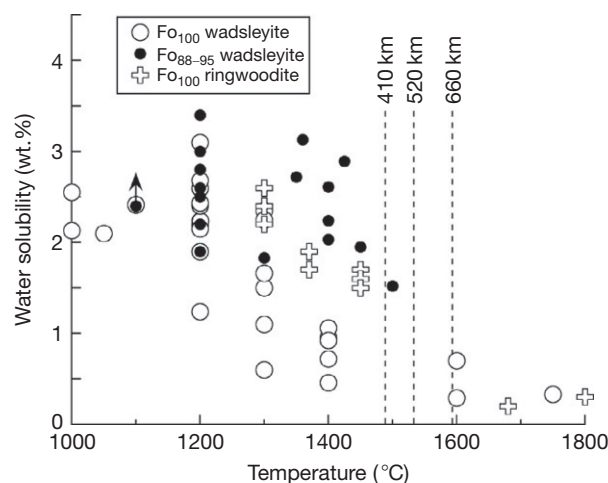


Figure 14 Water contents in wadsleyite and ringwoodite as a function of temperature. Open circles are data for Fe-free hydrous wadsleyite from Inoue et al. (1995), Kohn et al. (2002), Litasov and Ohtani (2003), Demouchy et al. (2005), and Jacobsen et al. (2005). Filled circles are data for Fe-bearing wadsleyite from Kawamoto et al. (1996), Kohlstedt et al. (1996), Smyth et al. (1997), Smyth and Kawamoto (1997), and Chen et al. (2002). Crosses are data for Fe-free hydrous ringwoodite from Ohtani et al. (2000). Estimated temperatures at the 410, 520, and 660 km discontinuities are from Katsura et al. (2004). Based on these data, at conditions of the transition zone, the water-storage capacity of wadsleyite would range between 1.5 and 3.0 wt.%. The corresponding value for ringwoodite is expected to be slightly lower (see text for discussion).

coefficient of $\sim 3.7 \pm 0.5$ in $(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$ at ~ 12.2 GPa and 1200 °C. Most recently, Férot and Bolfan-Casanova (2012) reported FTIR data consistent with $D^{\text{Wad-Ol}}$ of 4.7 ± 0.7 at 13.5 GPa and 1400 °C. The latter range of $D^{\text{Wad-Ol}}$ values therefore suggests that wadsleyite could contain between 2 and 3 wt.% H_2O in the transition zone. As shown in Figure 14, hydrous wadsleyite synthesized at 13–18.5 GPa over a range of temperature conditions contains up to ~ 3 wt.% water, very close to the limit originally suggested on crystal structure grounds by Smyth (1987). Although insensitive to pressure, water solubility in wadsleyite decreases with increasing temperature (e.g., Demouchy et al., 2005) (Figure 14).

Inoue et al. (1998) and Ohtani et al. (2000) reported water solubility in Fe-free ringwoodite of >2.2 wt.% at 19–23 GPa and 1300–1450 °C, in agreement with the measurements of Kohlstedt et al. (1996) on Fe-bearing ringwoodite at 19.5 GPa and 1100 °C. As shown in Figure 14, the water content of Fe-free ringwoodite tends to decrease with increasing temperature in a similar manner to Fe-free wadsleyite, reaching contents of 0.3 wt.% at 1800 °C (Ohtani et al., 2000). The temperature dependence for Fe-bearing ringwoodite is currently unknown. Given the similarity of results for Fe-free wadsleyite and Fe-free ringwoodite, however, one may reasonably expect similar water-storage capacity for the corresponding Fe-bearing phases, that is, slightly higher than for the Fe-free phases. Consequently, in a mantle of peridotite composition, the water-storage capacity of ringwoodite should be similar to but slightly smaller than that of wadsleyite. This is confirmed by measurements of the H_2O partition coefficient $D^{\text{Wad-Ring}}$, which is ~ 2 (Deon et al., 2011; Inoue et al., 2010).

In order to calculate the effect of water on the transformation, we require the partial molar free energies of Mg_2SiO_4 and Fe_2SiO_4 components in the hydrated wadsleyite solid solution.

At low concentrations of OH, the solution of this component will be in the Henry's law region, where its only effect on the major components is entropic. In that case, the chemical potentials of Mg_2SiO_4 and Fe_2SiO_4 components are given by

$$\mu_{\text{Mg}_2\text{SiO}_4}^{\text{Wd}} = \mu_{\text{Mg}_2\text{SiO}_4}^{\text{O}} + RT \ln \left(X_{\text{Mg}}^2 \cdot \gamma_{\text{Mg}} \cdot (1 - X_{\text{OH}})^{0.5} \right) \quad [7a]$$

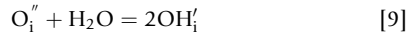
$$\mu_{\text{Fe}_2\text{SiO}_4}^{\text{Wd}} = \mu_{\text{Fe}_2\text{SiO}_4}^{\text{O}} + RT \ln \left(X_{\text{Fe}}^2 \cdot \gamma_{\text{Fe}} \cdot (1 - X_{\text{OH}})^{0.5} \right) \quad [7b]$$

In eqns [7a] and [7b], X_{Mg} and X_{Fe} refer to atomic fractions of magnesium and iron, respectively, on the large cation positions, while X_{OH} is the fraction of protonated O1 atoms. The standard state chemical potentials $\mu_{\text{Mg}_2\text{SiO}_4}^{\text{O}}$ and $\mu_{\text{Fe}_2\text{SiO}_4}^{\text{O}}$ refer to the free energies of the pure end-member wadsleyite at the pressure and temperature of interest. The activity coefficients for the Mg-Fe sites, γ_{Mg} and γ_{Fe} , refer to nonideal Mg-Fe mixing, combined with (nominally) ideal mixing of vacancies, which have a concentration

$$V_{\text{Mg}}'' = \frac{1}{8} X_{\text{OH}} \quad [8]$$

Equations [7] and [8] enable calculation of the effect of water on the two major components, given the assumptions of random mixing of OH groups with O1 and of vacancies with Mg and Fe. The nonideal part of Mg-Fe mixing was obtained by assuming a symmetric interaction parameter W_{MgFe} of $4.0 \text{ kJ g}^{-1} \text{ atom}^{-1}$ (Akaogi et al., 1989).

For olivine, Bai and Kohlstedt (1993) found H-solubility data to be consistent with formation of complexes between H and interstitial O atoms. In Kröger-Vink notation, this may be represented in simplified form as



Calculation of the chemical potentials of Mg_2SiO_4 and Fe_2SiO_4 components in the partially hydrated olivine, relative to water-free olivine under the same conditions of intensive variables, is obtained from

$$\mu_{\text{Mg}}^{\text{Ol}} = \mu_{\text{Mg}_2\text{SiO}_4}^{\text{O}} + RT \ln \left(\frac{X_{\text{Mg}}^2 \cdot \gamma_{\text{Mg}} \cdot (1 - X_{\text{OH}})^4}{(1 - 0.5X_{\text{OH}})^4} \right) \quad [10a]$$

$$\mu_{\text{Fe}}^{\text{Ol}} = \mu_{\text{Fe}_2\text{SiO}_4}^{\text{O}} + RT \ln \left(\frac{X_{\text{Fe}}^2 \cdot \gamma_{\text{Fe}} \cdot (1 - X_{\text{OH}})^4}{(1 - 0.5X_{\text{OH}})^4} \right) \quad [10b]$$

Activity coefficients γ_{Mg} and γ_{Fe} were calculated from the symmetric solution model using the experimentally measured interaction parameter of Wisser and Wood (1991) adjusted to 14 GPa from the excess volumes on the forsterite-fayalite join, giving a value of $5.0 \text{ kJ g}^{-1} \text{ atom}^{-1}$.

The combined effect of water and iron on the olivine-wadsleyite transition is calculated by fixing the bulk Fe/(Fe+Mg) and water content of mantle olivine at a point just above the depth where wadsleyite appears and then calculating the shift in equilibrium pressure relative to the value for pure anhydrous Mg_2SiO_4 . Proportions of phases through the two-phase region were calculated as follows: The Fe/(Fe+Mg) ratio of the olivine was set to a value less than or equal to the value just above the transition zone. The Fe/(Fe+Mg) ratio of the coexisting wadsleyite was obtained from the partitioning data of Katsura and Ito (1989). Then, from the Fe/(Fe+Mg) of the

initial mantle olivine, phase proportions were simply solved from the lever rule. Given proportions of olivine and wadsleyite, the concentrations of water in the two phases were calculated using a fixed water content of olivine above the transition zone and fixing the H_2O partition coefficient at either 10:1 or 5:1 in favor of wadsleyite (see in the preceding text). The equilibrium pressure was then calculated from (see Wood, 1995):

$$(P - P^{\circ})\Delta V^{\circ} = -RT \ln \left(\frac{X_{\text{Mg}}^2 \cdot \gamma_{\text{Mg}} \cdot (1 - X_{\text{OH}})^{0.5}}{(1 - 0.5X_{\text{OH}})^4} \right)_{\text{Ol}}^{\text{Wad}} + RT \ln \left(\frac{X_{\text{Mg}}^2 \cdot \gamma_{\text{Mg}} \cdot (1 - X_{\text{OH}})^4}{(1 - 0.5X_{\text{OH}})^4} \right)_{\text{Ol}} \quad [11]$$

where P° refers to the equilibrium pressure for the end-member reaction:



ΔV° refers to the volume change of this reaction at the P - T conditions of interest. Wood and Corgne (2007) performed the calculations at 1773 K and took P° to be 14.5 GPa (Figure 16).

In calculating the results shown in Figure 16, Wood and Corgne (2007) initially assumed that the ratio of water contents (by weight) in wadsleyite to olivine is 10:1 (following Wood, 1995) and repeated the calculation using a value of 5:1 and the correction to Kohlstedt et al.'s (1996) results (see Section 2.04.4.1). The results indicate that small amounts of water act to lower the pressure of the transformation and broaden it. If mantle olivine contains 1000 ppm H_2O by weight, the transformation would shallow by up to 10 km and broaden substantially. The results of Wood (1995), shown in Figure 16(a), indicate that, given a transition interval in the anhydrous system of about 7 km (Helffrich and Wood, 1996), 500 ppm H_2O in mantle olivine would broaden the transformation to over 20 km. He argued that, given seismological observations at high frequency, which imply that the 410 km discontinuity is < 10 km wide (Benz and Vidale, 1993; Paulssen, 1988; Yamazaki and Hirahara, 1994), the H_2O content of mantle olivine is constrained to be < 200 ppm. As shown by Wood and Corgne (2007), this constraint is relaxed by a factor of about 2 if the partition coefficient for H_2O between wadsleyite and olivine is 5, rather than 10 (Figure 16(b)). Thus, using recent water partitioning data (Chen et al., 2002; Deon et al., 2011; Férot and Bolfan-Casanova, 2012), about 400 ppm of H_2O is the calculated upper limit for mantle olivine under conditions of the 410 km discontinuity (Figure 16(b)) if the transformation interval is 10 km wide. Smyth and Frost (2002) and Frost and Dolejs (2007) have confirmed experimentally that the olivine-wadsleyite transformation is broadened and shallowed by the addition of H_2O , in line with the predictions made by Wood (1995). However, Frost and Dolejs (2007), who performed experiments at H_2O saturation, concluded that the effect of H_2O is actually much smaller than that calculated by Wood and Corgne (2007). The potential errors in our model are firstly that $D^{\text{Wad-Ol}}$ for H_2O could be smaller than the value of five assumed in Figure 16(b) and secondly that the solution models of H_2O in wadsleyite and olivine are wrong. Our $D^{\text{Wad-Ol}}$ is very close to the

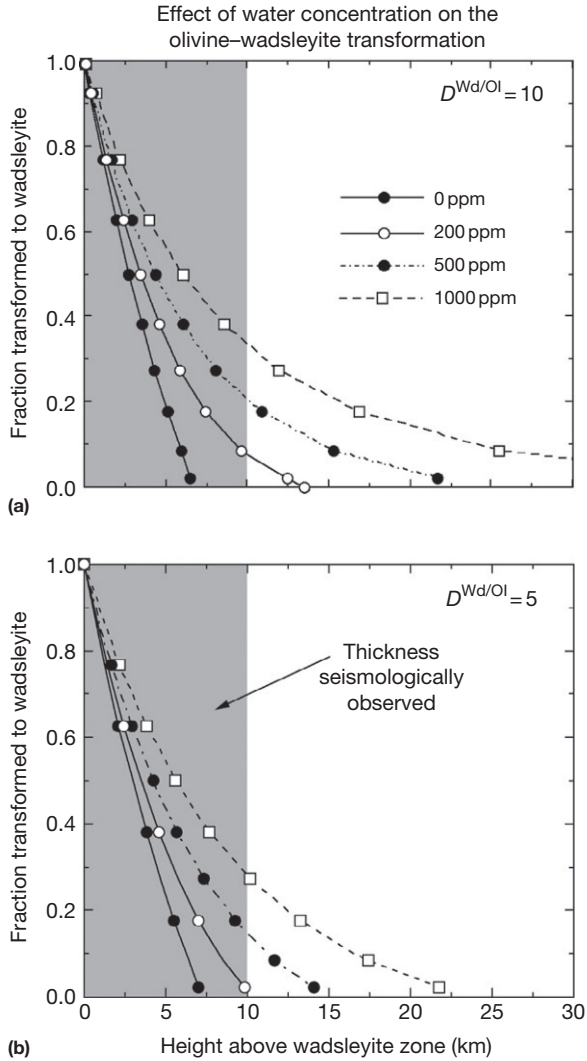


Figure 16 Figure showing the calculated depth interval of the olivine–wadsleyite phase transformation for initial H₂O contents of olivine of 0, 200, 500, and 1000 ppm by weight assuming that the OH defects and vacancies are completely disordered in the lattice. Water is assumed to be concentrated in wadsleyite relative to olivine by a factor of 10 in (a) and a factor of 5 in (b). Given a seismologically determined transformation interval of less than about 10 km (gray area), calculated maximum H₂O contents are 200 ppm (a) and ~400 ppm (b). Note that experiments with ~10 000 ppm H₂O in wadsleyite (Frost and Dolejs, 2007) generated a much smaller effect than calculated with this model, probably because of ordering of defects at high concentration.

most recent measurements of Férot and Bolfan-Casanova (2012), however, so the first explanation is unlikely. Most probably, at H₂O saturation, the concentration of defects in wadsleyite is so high that the magnesium vacancies and OH groups cluster, thus reducing the entropic effect calculated from eqns [7a] and [7b] (Frost and Dolejs, 2007). This conclusion, with which we concur, does not mean that our model is wrong however, except at very high H₂O concentrations. At low concentrations of H₂O and vacancies, any vacancy–OH clusters must dissociate and the entropy of solution must approach that given by our equations. Thus, at realistic

H₂O concentrations (hundreds of ppm) in the mantle the disordered model of eqn [7] may still be a reasonable approximation.

Seismological evidence for the presence of H₂O at the 410 km discontinuity has to some extent focused on regions where broadening of the discontinuity may be detected. Van der Meijde et al. (2003) had, for example, investigated P-to-S conversions from the 410 km discontinuity in the Mediterranean region, which has a long history of subduction and possible introduction of water into the mantle. They find broadening of the 410 km discontinuity to between 20 and 35 km, consistent with about 700 ppm ($D^{Wd-Ol}=10$) to 1500 ppm ($D^{Wd-Ol}=5$) H₂O in olivine. The 660 km discontinuity is, in contrast, sharp and apparently unaffected by the long period of active subduction.

If we accept that the width of the 410 km discontinuity can constrain the water content of the mantle olivine, then we obtain maximum values of around 400 ppm with, given the seismological study discussed in the preceding text, regional variations up to a factor of ~4 greater. It is interesting to note that these values are in very good agreement with upper-mantle H₂O contents inferred from the water contents of MORBs. As discussed earlier, the latter lead to 80–180 ppm H₂O in the depleted source regions of N-MORB, 200–950 ppm in the source regions of E-MORB, and 1000–3000 ppm in the mantle sources of back-arc basin basalts.

2.04.4.2.3 Slab dehydration and seismicity

In addition to nominally anhydrous minerals such as olivine and its high-pressure polymorphs, it has been shown experimentally that water could be held in the mantle under hydrous conditions at low temperatures in a variety of OH-bearing silicates collectively known as dense hydrous magnesium silicates (DHMS) (e.g., Angel et al., 2001; Ohtani et al., 2000). These phases can be present in subducting lithosphere at depths greater than about 250 km if sufficient water is available. The petrologic and thermal nature of subducting slabs is, however, key to water transfer at depths (van Keken et al., 2011). Hot subducting slabs should be completely dehydrated by 150 km depth, whereas mineralogically bound water can be transported efficiently to >200 km through old and fast subduction zones, thereby providing a possible pathway for significant amounts of water to enter the deep mantle (van Keken et al., 2011). However, because there is no obvious seismicity associated with the predicted dehydration of nominally anhydrous olivine polymorphs and DHMS, it has been argued that subducting slabs are essentially dry at depths below 400 km and thus do not provide significant amounts of water to the mantle transition zone and the lower mantle (Green et al., 2010).

2.04.4.3 Transition Zone Water Filter

Bercovici and Karato (2003) used the observation that the major minerals of the transition zone, wadsleyite and ringwoodite, dissolve substantially more H₂O than those of the upper mantle (above 410 km depth) and lower mantle (below 660 km) to suggest that the transition zone is very rich in H₂O and that the 410 km acts as a ‘water filter’ for trace elements. They argue that, provided the transition zone is richer in H₂O

than the solubility limit of the mantle at 410 km depth, upwelling mantle in the transition zone must release H₂O as it crosses from the wadsleyite to olivine stability field at 410 km. At an approximate temperature of 1500 °C, this water would not exist as a fluid, as shown schematically in Figure 15, but as a hydrous silicate melt. Partial melting would strip most of the incompatible trace elements out of the solid mantle traversing the 410 km discontinuity, and, provided the melt was left behind 'perched' on the discontinuity, the residual solids could, in the upper mantle, provide the trace element-depleted source region of N-MORB. Furthermore, melting could generate a much sharper discontinuity than that calculated for subsolidus conditions in the preceding text, even for quite high water concentrations. The melt, which must be denser than the solid mantle to be left behind at the discontinuity, would be recycled back into the lower mantle at subduction zones where it would freeze and attach itself to descending plates.

Bercovici and Karato's mechanism for generating an upper mantle depleted in incompatible elements is attractive in that it provides the possibility of producing depleted (upper) and enriched (lower) reservoirs without invoking strictly layered mantle convection. It can also be disproven, because it is based on a number of assumptions which are experimentally testable. Firstly, the partitioning of elements between the solid phases at 410 km depth and hydrous silicate melts must be consistent with the pattern of trace element depletion of the MORB source region. The available experimental data (Mibe et al., 2006) suggest that the model passes this test. Secondly, the hydrous melts must be denser than the mantle above 410 km depth. And thirdly, the storage capacity of the upper mantle must be very low in order to generate the water-depleted (80–180 ppm) source regions of N-MORB. Based on recent partitioning and solubility measurements for H₂O in mantle minerals, Hirschmann et al. (2009) argued that the water concentration of the mantle just above the 410 km discontinuity (i.e., following 'water-filtering') would be at least 500 ppm, which is more than three times the expected value for N-MORB sources. This observation is difficult to reconcile with the 'water-filter' hypothesis. Nevertheless, the derived water concentration would be consistent with the range estimated in the enriched source regions of E-MORBs and OIBs (up to 1000 ppm), suggesting that dehydration melting near the base of the upper mantle may occur in specific settings. This would be consistent with seismological evidence for the existence of a low-velocity layer, plausibly a dense partial melt, on top of the 410 km discontinuity in the northwestern United States (Schmandt et al., 2011; Song et al., 2004). Seismic constraints on the extent and the nature of the low-velocity layer remain the subject of debate, however (e.g., Hier-Majumder and Courtier, 2011; Schmandt et al., 2011; Tauzin et al., 2010). Furthermore, it has been argued that hydrous melts required by the 'water-filter' model would not be sufficiently dense to remain stable at 410 km depth (Hirschmann, 2006; Hirschmann et al., 2009). High-pressure density measurements by Sakamaki et al. (2006) indicate however, that hydrous melt could be gravitationally stable at 410 km depth but only if it contains <6.7% H₂O. The latter H₂O concentration is about half the concentration expected in the hypothetical melt layer (Hirschmann et al., 2009), which casts doubt on

its stability at 410 km depth. In order to progress further with this hypothesis, more data are required to evaluate the influence of the major element concentrations in the melt (FeO and CaO) and the effect of temperature (e.g., Hirschmann et al., 2009) on the densities of possible hydrous melts.

The current status of the 'water-filter' hypothesis is that it appears consistent with the available trace element partitioning data but that it is inconsistent with current melt density measurements and the low H₂O concentrations in the N-MORB source region. Since, however, there is seismic evidence for a low-velocity zone on top of the 410 km discontinuity in some regions and the high-pressure density data for hydrous melts are quite limited, the 'water-filter' hypothesis appears to merit further experimental and seismological investigation.

2.04.4.4 Water Solubility in Lower-Mantle Minerals

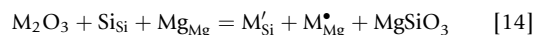
The water-storage capacity of the lower mantle has remained controversial due to the difficulties of synthesizing suitable samples (free of impurities and water saturated) and analyzing them. Some studies (Litasov et al., 2003; Murakami et al., 2002) reported large water-storage capacities for MgPv (~1400–2000 ppm), ferropericlasite FP (~2000 ppm), and CaPv (~4000 ppm) in peridotite. On the other hand, Bolfan-Casanova et al. (2000, 2002, 2003) reported water contents in MgPv and FP to be <10 and 20–75 ppm, respectively, implying that, if the mantle contains several hundred ppm H₂O, this cannot be stored in the nominally anhydrous minerals of the lower mantle.

2.04.4.4.1 Magnesium silicate perovskite

Navrotsky (1999) suggested that the incorporation of trivalent cations (hereafter M³⁺) such as Al³⁺ and Fe³⁺ enhances the solubility of hydrogen in magnesium silicate perovskite. Assuming M³⁺ substitutes for Si⁴⁺ (B-site) in MgPv and is charge-balanced via formation of an oxygen vacancy, we can write the following reaction for dissolution of M₂O₃ (in Kröger–Vink notation):

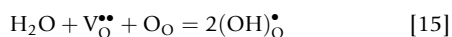


Alternatively, if M³⁺ enters MgPv via coupled substitution in both A- and B-sites, we can write the reaction as



As inferred from MgPv–melt partitioning data in peridotite composition (Liebske et al., 2005), ~90% of Al³⁺ (and ~40% Cr³⁺) enter the B-site of MgPv. In contrast, Fe³⁺, which is larger, should be predominantly present in the A-site, thus charge balancing some of the Al³⁺ in the B-site according to reaction [14]. Assuming 60% of Fe in MgPv is Fe³⁺ (e.g., Frost et al., 2004; McCammon et al., 1997) and Fe³⁺ enters only the A-site (e.g., Vanpeteghem et al., 2006), one can estimate that in MgPv containing 4–5 wt.% Al₂O₃, and 7 wt.% FeO* as expected in the mantle (e.g., Nishiyama and Yagi, 2003; Wood, 2000) about 80–95% of Al³⁺ would be charge-balanced by Fe³⁺ in the A-site. Therefore, ~5–20% of the Al³⁺ present could be charge-balanced by formation of oxygen vacancies. This estimate leads to ~0.06–0.3% of the oxygen

sites in MgPv being vacant. These vacancies would plausibly interact with H₂O as follows:



Then, as shown in Figure 17, one can derive a maximum water solubility of between 0 and 2200 ppm in MgPv taking account of the uncertainty in the Fe³⁺/Fe ratio (60 ± 5%). Increasing the proportion of Fe³⁺ in the B-site increases the number of oxygen vacancies and the anticipated water solubility. For example, if 20% of Fe³⁺ is actually present in the B-site, the derived water content would be ~2200–4200 ppm (Figure 17). The water contents of MgPv estimated by Murakami et al. (2002) and Litasov et al. (2003) are broadly consistent with this model of hydroxylation of oxygen vacancies. This is also in agreement with recent experiments by Inoue et al. (2010), which indicate water solubility in Al-free perovskite of up to about 1000 ppm. The results of Bolfan-Casanova et al. (2003) on similar bulk compositions as the ones used in the studies of Murakami et al. (2002) and Litasov et al. (2003) indicate about two orders of magnitude lower solubility of H₂O in Mg-perovskite, however. Currently, the large differences between these studies of (nominally) the same problem are unresolved, and there is clearly a need for improvement of both synthesis and analytical methods.

2.04.4.4.2 Calcium silicate perovskite

In peridotite, CaPv contains minor amounts of Mg, Al, and Fe (e.g., Kesson et al., 1998; Wood, 2000). Based on the partitioning parabolas obtained by Corgne et al. (2005), it is reasonable to assume that Al enters only the B-site. Therefore, the fraction of oxygen vacancies required for charge compensation depends on the proportion and site occupancy of ferric iron. Considering Al₂O₃ and FeO* contents of 1 wt.% and 1–2 wt.%, respectively, as representative of the CaPv composition in the lower mantle (e.g., Kesson et al., 1998; Wood, 2000), ~0.6–1% of oxygen positions are required to be vacant for charge

compensation if Fe is assumed to be only Fe³⁺ and to enter only the B-site. In this case and if all the oxygen vacancies created are filled by hydroxyl groups according to reaction [15], we derive a maximum water content of ~3000–4300 ppm consistent with the measurements of Murakami et al. (2002). This value is halved (~1750 ppm) if Fe is only Fe²⁺ and located in the A-site. However, Fe is likely to be present in CaPv as both Fe²⁺ and Fe³⁺ with Fe²⁺ and probably most of the Fe³⁺ in the A-site. As shown in Figure 18, water solubility decreases with increasing FeO* content and decreasing proportion of Fe³⁺ in the B-site, the decrease being more pronounced at high Fe³⁺/Fe ratio. For example, water solubility would be zero for CaPv contents above 1.8 wt.% FeO* and Fe³⁺/Fe ratio above 0.8. Assuming that ~60% Fe is Fe³⁺, as in MgPv, water contents would be ~250–1000 ppm if Fe³⁺ is only in the A-site and ~700–1250 ppm if 15% of Fe³⁺ is in the B-site (Figure 18).

2.04.4.4.3 Ferropericlasite

Potential mechanisms of H₂O dissolution in (Mg,Fe)O ferropericlasite are similar to those outlined for perovskite in the preceding text. Currently, however, large discrepancies in the data for H₂O solubility in this phase (<100 ppm, Bolfan-Casanova et al., 2003; Litasov, 2012; 2000 ppm, Murakami et al., 2002) make further discussion and comparison with perovskite meaningless.

2.04.5 Conclusions

Partitioning of trace elements between the high-pressure phases of the transition zone and lower mantle and coexisting silicate melts has been found to obey the simple elastic strain model that has been successfully applied to a wide range of low-pressure minerals (Blundy and Wood, 1994). For elements of fixed charge, solid–liquid partition coefficients D_i are an approximately parabolic function of ionic radius, where the

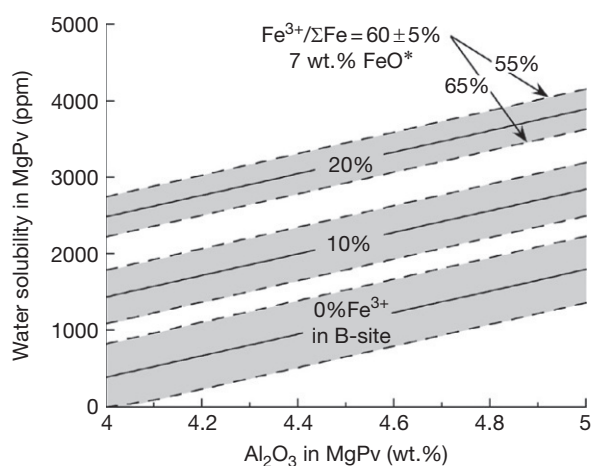


Figure 17 Maximum water solubility in MgPv as function of Al₂O₃ content. The calculation assumes that MgPv contains 7 wt.% FeO* in the lower mantle and that hydroxyl groups occupy oxygen vacancies created to charge-balance Al³⁺ in the B-site (reaction [20]). At a given Al₂O₃ content, water solubility increases with increasing the amount of Fe³⁺ in the B-site and with increasing Fe³⁺/ΣFe ratio. See text for discussion.

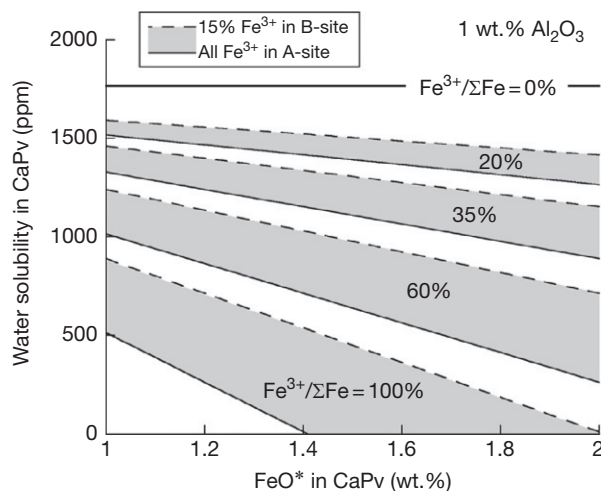


Figure 18 Estimated water solubility in CaPv as function of FeO* content. The calculation assumes that CaPv contains 1 wt.% Al₂O₃ in the lower mantle and that hydroxyl groups occupy oxygen vacancies created to charge-balance Al³⁺ in the B-site (reaction [15]). At a given FeO* content, water solubility increases with increasing the amount of Fe³⁺ in the B-site and with decreasing Fe³⁺/ΣFe ratio. See text for discussion.

peak of the parabola D_0 corresponds to the partition coefficient for the ion that enters the site without strain. One marked difference from low-pressure minerals such as clinopyroxene and plagioclase is that many elements that are very incompatible in shallow mantle and crustal minerals are very compatible in the perovskites of the lower mantle (Figures 5 and 8). In Figure 5, for example, it can be seen that Zr and Hf have partition coefficients into MgPv that are > 1 , while U and Th have partition coefficients into CaSiO_3 perovskite of larger than ten (Figure 8). As can be seen from Figure 8, Th^{4+} and U^{4+} are markedly and very unusually more compatible in the Ca-site of perovskite than Ca^{2+} itself.

The investigation of the limits of Henry's law for Ca-perovskite (in the form of the low-pressure-phase CaTiO_3) demonstrates that the high partition coefficients for $3+$ and $4+$ ions into the Ca^{2+} site arise from the ease with which excess charge is compensated in the perovskite structure. This takes place by the creation of cation vacancies. Thus, the compositional dependence of Th partitioning indicates that Th^{4+} replaces 2Ca^{2+} with the creation of a vacancy in the Ca sublattice.

The measured liquid–solid partition coefficients have been used to investigate the possibility that the mantle underwent gross stratification early in Earth history, with establishment of a lower layer rich in majorite or perovskite. Applying the constraint that the primitive ‘upper’ mantle has approximately chondritic ratios of the RLEs, we find that the permissible extents of high-pressure fractionation are very small. Thus, for example, fractionation of perovskite into the lower mantle is limited to about 8% of mantle volume (Figure 13). The limit of possible majorite fractionation (in the absence of perovskite fractionation) is 4%. This does not mean that extensive melting and fractional crystallization of the mantle did not occur in early Earth history. It means only that later rehomogenization of the mantle has erased virtually all record of any such event and that only a few percent of the lower-mantle volume can, at most, remain isolated from the upper mantle. This result is robust provided that there is not a very strong negative pressure effect on partitioning of ‘incompatible’ trace elements such as U and Th into perovskites.

Experimentally and analytically, the behavior of H in high-pressure phases is much more difficult to constrain than that of other trace elements. Much of the available data show appreciable scatter. Nevertheless, it is apparent that wadsleyite and ringwoodite of the transition zone can dissolve H_2O at levels larger than 2 wt.% (Figure 14), while the maximum solubility in the low-pressure olivine polymorph is about 0.5 wt.% (Hirschmann et al., 2005). Given that H_2O partitions between wadsleyite and olivine with a ratio on the order of 5:1, it can be shown that the width of the 410 km discontinuity places constraints on the water content of the mantle (Figures 15 and 16). In the absence of melting, the seismologically determined sharpness of the 410 km discontinuity, which corresponds to the olivine–wadsleyite phase transformation, fixes the maximum water content of the mantle olivine at about 400 ppm provided the OH defects and vacancies are disordered in wadsleyite at low H_2O concentrations. This limit of 400 ppm is in broad agreement with mantle water contents estimated from H_2O contents in MORBs.

Water solubilities in the principal minerals of the lower mantle, ferropericlase, magnesium, and calcium silicate perovskites, are very poorly known. Currently available data vary by almost two orders of magnitude from a few tens of parts per million to a few thousand parts per million. It is clear, however, that whichever data are accepted, H_2O is much more soluble in the transition zone than in the lower mantle. These observations have led to the suggestion of Bercovici and Karato (2003) that the transition zone is water-rich, while the upper and lower mantles are relatively dry. According to this idea, the depleted upper mantle is generated by hydrous partial melting of upwelling fertile mantle as it crosses the 410 km discontinuity. Measured densities of hydrous melts at appropriate conditions (Matsukage et al., 2005; Sakamaki et al., 2006) indicate, however, that such melts are unlikely to remain perched on the 410 km discontinuity as the depleted solid mantle rises. The depleted mantle should also be much richer in H_2O (> 500 ppm) than appears plausible from the H_2O concentrations in N-MORB source region (200 ppm).

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2.05 Mineralogy of the Deep Mantle – The Post-Perovskite Phase and its Geophysical Significance

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Glossary

CMB The core–mantle boundary is the surface defined by the contrast in composition between silicate and oxide crystalline rocks in the mantle and molten iron alloy in the core.

D'' Designation for the lowermost 200–300 km of the lower mantle. This region is distinct from the overlaying mantle in

that the seismic velocity variations are not consistent with homogeneous material under self-compression and an adiabatic temperature gradient.

DAC Diamond-anvil cell compression devices in which a sample is compressed between faceted diamonds, often with laser heating, to achieve high *P–T* conditions such as in the lower mantle and core.

2.05.1 Lower Mantle Mineralogy

The Earth's uppermost mantle is peridotitic (pyrolytic) in composition based on petrologic evidence (McDonough and Sun, 1995). Given that the global seismic velocity discontinuity observed at 410 km depth can be reconciled with a phase transition from olivine to wadsleyite, the transition zone should also be peridotitic in composition, although it could be contaminated by subducted former oceanic lithosphere with an eclogitic component (e.g., Irifune et al., 2008; Nishihara et al., 2005). On the other hand, the chemical composition of the lower mantle is a matter of ongoing debate. It is generally believed that the bulk Earth composition is similar to

solar abundance or the nonvolatile element composition of primitive meteorites (CI chondrites). If this is the case, the Mg/Si ratio of the Earth's mantle should be close to 1.0, while the peridotitic upper mantle shows Mg/Si = 1.27, with Mg₂SiO₄ olivine as the most abundant mineral. In order to reconcile the chondritic Earth model with the peridotitic mantle, Allègre et al. (1995) proposed 5 wt% Si in the core as its primary light alloy component. Alternatively, the lower mantle could be Si-enriched relative to the upper mantle and composed primarily of MgSiO₃-rich perovskite.

Recent experimental and geophysical modeling studies have supported a perovskitic lower mantle. Riccolleau et al. (2009) argued that the Preliminary Reference Earth Model (PREM)

density profile of the lower mantle is compatible with single-phase perovskite, on the basis of P - V - T (pressure–volume–temperature) equation of state (EoS) of MgSiO_3 -rich perovskite formed in a natural peridotite bulk composition. However, the chemical composition of MgSiO_3 -rich perovskite may have changed with changing P - T conditions during their measurements because it coexisted with $(\text{Mg,Fe})\text{O}$ ferropericlase in the sample. More recently, Murakami et al. (2012) measured shear-wave velocities of MgSiO_3 perovskite and MgO to 91 GPa and 2700 K and also estimated the effects of Al and Fe impurities for room-temperature measurements to 124 GPa. Comparing the velocities of (Fe,Al) -bearing MgSiO_3 perovskite and $(\text{Mg,Fe})\text{O}$ ferropericlase to the PREM velocity profile, Murakami et al. concluded that the lower mantle is composed of more than 93% MgSiO_3 -rich perovskite, consistent with a chondritic lower mantle model rather than a peridotitic mantle model. First-principles studies spanning two decades not only support a peridotitic uppermost lower mantle but also suggest that PREM (Dziewonski and Anderson, 1981) velocities deviate from a peridotitic composition in the deeper lower mantle (da Silva et al., 2000; Karki et al., 2001; Wentzcovitch et al., 2004, 2009; Zhang et al., 2014). Part of the deviation is likely to be related with the post-perovskite transition (Wentzcovitch et al., 2004). Thermodynamic modeling also suggests deviations from a peridotitic mantle (Xu et al., 2008), while a more recent first-principles molecular dynamics (MD) gives additional support to a peridotitic lower mantle (Zhang et al., 2014).

Regardless of this evolving mineral physics perspective, it is widely believed that the whole mantle is being mixed and the lower mantle is thus commonly inferred to be similar in composition to the peridotitic upper mantle. The experiments by Irifune et al. (2010) using multianvil apparatus with sintered diamond anvils showed phase assemblage and proportion in a peridotitic lower mantle to 47 GPa and 2073 K to be 74 vol.% MgSiO_3 -rich perovskite, 18 vol.% ferropericlase, and 8 vol.% CaSiO_3 perovskite. Kesson et al. (1998) demonstrated through a combination of diamond anvil cell (DAC) experiments and chemical analysis using transmission electron microscope (TEM) that a peridotitic deep lower mantle should consist of 69 wt% MgSiO_3 -rich perovskite, 22 wt% ferropericlase, and 9 vol.% CaSiO_3 perovskite. With similar techniques, Murakami et al. (2005) reported 72 vol.% post-perovskite, 21 wt% ferropericlase, and 7 wt% CaSiO_3 perovskite for P - T conditions in the lowermost mantle. Trampert et al. (2004) found, however, that the proportion of MgSiO_3 -rich perovskite is variable by up to $\pm 10\%$ in the lower mantle. The lower mantle is probably primarily (69–93 wt%) MgSiO_3 -rich perovskite, so the stability and property of this phase have been extensively studied.

2.05.2 Post-Perovskite Phase

2.05.2.1 Discovery

Silicate perovskite was first synthesized at 30 GPa based on laser-heated DAC technique by Liu (1974). Since then, MgSiO_3 -rich perovskite is known to be a primary constituent in the lower mantle, consisting about 70% of a peridotitic lower mantle as noted earlier in the text, coexisting with minor amounts of $(\text{Mg,Fe})\text{O}$ ferropericlase and CaSiO_3

perovskite (Hirose, 2002; Irifune, 1994; Wood, 2000). While seismology has shown that the lowermost few hundred kilometers of the mantle, called the D'' layer, has distinct properties and a widespread seismic velocity discontinuity (Lay and Helmberger, 1983), it was initially believed that MgSiO_3 -rich perovskite is stable down to the core–mantle boundary (CMB). Indeed, Knittle and Jeanloz (1987) reported the stability of orthorhombic $(\text{Mg,Fe})\text{SiO}_3$ perovskite up to 127 GPa, close to the D'' conditions. Subsequent experimental and theoretical studies supported the stability of MgSiO_3 -rich perovskite into the deep lower mantle (e.g., Andraut, 2001; Fiquet et al., 2000; Karki et al., 2000; Kesson et al., 1998; Wentzcovitch et al., 1993). Some form of solid–solid phase transition with a positive Clapeyron slope in the lowermost mantle was suggested from the correlation between temperature-modulated velocity anomalies and elevation of the observed D'' S-wave velocity discontinuity, but this was speculative (Sidorin et al., 1999).

Conventionally, the identification of a high-pressure phase is made after the sample is recovered at ambient conditions. In the early 1990s, intense synchrotron x-rays became available to examine crystal structure *in situ* at high P - T (see a review by Yagi, 2007). Such *in situ* experiments are important in particular for metals because high-pressure forms of metal usually transform back to low-pressure forms during decompression. This is sometimes true for silicates as well. Indeed, MgSiO_3 post-perovskite cannot be quenched to ambient conditions as it converts to amorphous structure upon decompression; therefore, *in situ* observations were key to its discovery.

Murakami et al. performed x-ray diffraction (XRD) measurements *in situ* for the lowermost mantle P - T conditions, based on a combination of laser-heated DAC and synchrotron radiation at SPring-8. In 2002, they first observed a number of unknown diffraction peaks in the XRD patterns of natural peridotite composition at pressures higher than 120 GPa (Murakami et al., 2005). Subsequently, they analyzed MgSiO_3 and found similar radical changes in the XRD patterns when MgSiO_3 perovskite was heated to 2500 K at 127 GPa (Figure 1(a) and 1(b)) (Murakami et al., 2004). Importantly, such conversion was found to be reversible; the pattern changed back to that of perovskite when the sample was decompressed and reheated at 89 GPa (Figure 1(c)). These observations indicated a phase transition from MgSiO_3 perovskite to a new polymorph, now called post-perovskite.

The crystal structure of MgSiO_3 post-perovskite was determined with the aid of computational MD simulations (Murakami et al., 2004). The details of structure determination by MD calculations were reported in Hirose and Kawamura (2007). ‘Perovskite’ has a family of related structures with a vast range of chemical compositions. Nevertheless, the XRD peaks observed by Murakami et al. are not accounted for with any perovskite-type structure. Pressure-induced phase transformations from perovskite to denser structures were not known at that time. Tsuchiya et al. (2004b) independently obtained this structure using first-principles MD simulations with variable cell shape (Wentzcovitch et al., 1993) guided by a rationale based on pressure-induced structural distortion of perovskite (Wentzcovitch et al., 1995). The search was motivated by the XRD data of Murakami et al. (2004), which, together with thermodynamic stability calculations (Tsuchiya et al., 2005a), confirmed the nature of the identified structure

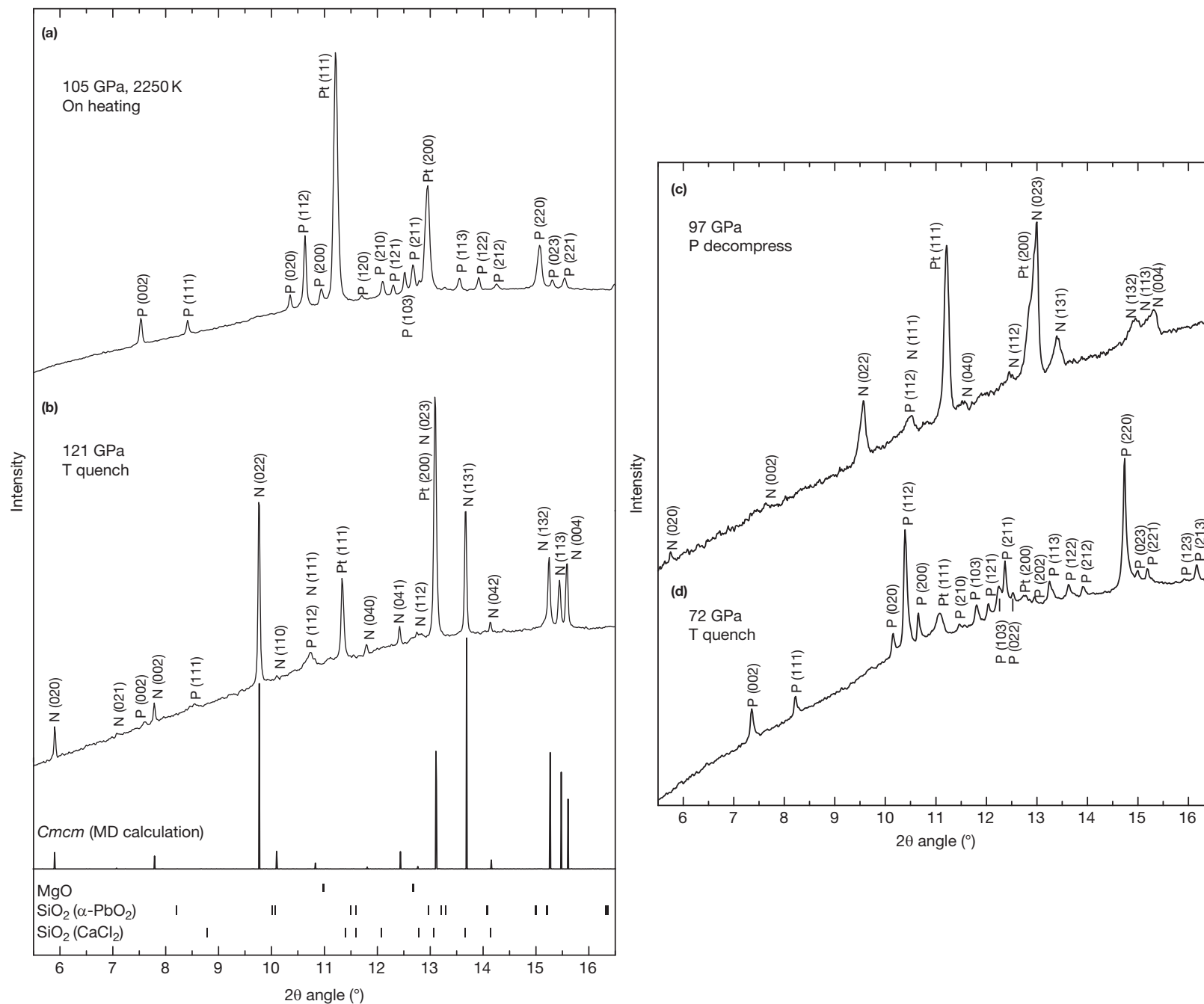


Figure 1 XRD patterns of MgSiO_3 . (a) Perovskite at 105 GPa and 2250 K, (b) post-perovskite at 121 GPa and 300 K after heating at 127 GPa, (c) post-perovskite at 97 GPa and 300 K after decompression from 125 GPa, and (d) perovskite at 72 GPa and 300 K after heating at 89 GPa (after Murakami et al., 2004). P, perovskite; Pt, platinum; N, new phase (post-perovskite). In (b), the calculated powder XRD pattern of post-perovskite (space group: $Cmcm$) and the peak positions of MgO and SiO_2 (both $\alpha\text{-PbO}_2$ -type and CaCl_2 -type structures) are shown.

at experimental conditions. The crystal structure of post-perovskite and the envisioned relationship between the perovskite and post-perovskite structures are illustrated in **Figure 2**. The coordination numbers of Si and Mg remain six and eight, respectively, as in perovskite. The Mg^{2+} site in post-perovskite is smaller than in perovskite, which results in a volume reduction of 1.0–1.5% (Litaka et al., 2004; Tsuchiya et al., 2004b). Oganov and Ono (2004) also obtained the same structure from the analogy of similar phase transition in Fe_2O_3 . This structure is the same as those of UFeS_3 (Noel and Padiou, 1976) and CaIrO_3 (McDaniel and Schneider, 1972), both of which are stable at ambient pressure.

2.05.2.2 Stability

Post-perovskite-type phase transitions have now been reported in a variety of simple and multicomponent systems: MgSiO_3 (Hirose et al., 2006a; Murakami et al., 2004; Oganov and Ono, 2004; Ono and Oganov, 2005; Shim et al., 2004; Tsuchiya et al., 2004a,b), MgGeO_3 (Hirose et al., 2005b), MnGeO_3 (Tateno et al., 2006), ZnGeO_3 (Yusa et al., 2005), CaIrO_3 (Hirose and Fujita, 2005; Kojitani et al., 2007), Al_2O_3 (Akber-Knutson et al., 2005; Caracas and Cohen, 2005; Oganov and Ono, 2005; Stackhouse et al., 2005a,b; Tsuchiya et al., 2005b), Fe_2O_3 (Ono and Ohishi, 2005; Ono et al., 2004), Mn_2O_3 (Santillán et al., 2006), NaMgF_3 (Martin et al., 2006; Umemoto et al., 2006a), and natural pyrolite (KLB-1 peridotite) (Grocholski et al., 2012; Murakami et al., 2005; Ohta et al., 2008a; Ono and Oganov, 2005), normal mid-ocean ridge basalt (MORB) compositions (Grocholski et al., 2012; Hirose et al., 2005a; Ohta et al., 2008a; Ono et al., 2005), harzburgite composition (Grocholski et al., 2012), and San Carlos olivine (Grocholski et al., 2012). CaIrO_3 has been often used as an analog of MgSiO_3 post-perovskite to explore

the Clapeyron slope of the perovskite/post-perovskite phase transition boundary (Hirose and Fujita, 2005; Kojitani et al., 2007), compression behavior (e.g., Martin et al., 2006), deformation mechanism (e.g., Walte et al., 2007, 2009), rheology (Hunt et al., 2009), grain growth (Yoshino and Yamazaki, 2007), etc., which are difficult to experimentally examine *in situ* for the lowermost mantle high P - T conditions.

2.05.2.2.1 Post-perovskite phase boundary in pure MgSiO_3

The determination of the thermodynamic post-perovskite boundary in MgSiO_3 post-perovskite is important to shed light on the nature of the D'' region. This is a challenging task for both experiments and computations for several reasons. *In situ* crystallography based on DAC has been extended to the multi-Mbar regime, and temperatures in these experiments have crossed the 6000 K mark. However, high P - T calibration standards still give uncertainties about the post-perovskite phase boundary. Computations based on density functional theory (DFT) (Hohenberg and Kohn, 1964; Kohn and Sham, 1965) suffer from uncertainties related with the choice of the approximation used to describe the exchange–correlation energy of electrons and of the approach used to describe ionic motion: quantum at relatively low temperatures or classical at relatively high temperatures.

The first report on MgSiO_3 post-perovskite by Murakami et al. (2004) found that it exists above 125 GPa and 2500 K, but did not tightly constrain the P - T location of the boundary. Later, Tateno et al. (2009) demonstrated on the basis of experiments to 171 GPa and 4400 K that the phase transition boundary between perovskite and post-perovskite in pure MgSiO_3 is located at 121 GPa corresponding to 2650 km depth at a plausible deep lower mantle temperature of 2400 K (Figure 3).

Recently, the accuracy of the pressure scale used to determine experimental pressure has been a matter of extensive debate (e.g., Fei et al., 2004; Hirose, 2007). With synchrotron XRD measurements, pressure at high temperature is calculated from the P - V - T EoS of an internal pressure standard loaded together with a sample. The typical pressure standards include Au, Pt, MgO, and NaCl. However, it is known that each standard indicates a different pressure, sometimes with differences of more than 10 GPa at ~ 120 GPa even at room temperature (Akahama et al., 2002; Hirose et al., 2008a; Matsui et al., 2009). Even using a given pressure standard, different EoSs show different pressures; for example, the EoS of Au proposed by Fei et al. (2007) gives pressure higher by about 12 GPa at 110 GPa/2400 K than that reported by Anderson et al. (1989) (Hirose et al., 2008a). On the other hand, Fei et al. (2007) proposed internally consistent pressure scales (EoSs) of Au, Pt, NaCl, and Ne primarily based on the MgO scale reported by Speziale et al. (2001). Similar efforts to establish consistent pressure scales are also found in Dorogokupets and Dewaele (2007).

The post-perovskite phase transition boundary in pure MgSiO_3 has been experimentally determined using different pressure standards of Pt, Au, and MgO (Hirose et al., 2006a; Ono and Oganov, 2005; Tateno et al., 2009) (Figure 3). These results reported transition pressures differing by more than 15 GPa, but this inconsistency can be explained by the difference in pressure scales. Ono and Oganov (2005) demonstrated that the transition occurred above 130 GPa and 2500 K based on the Pt scale proposed by Holmes et al. (1989). Such

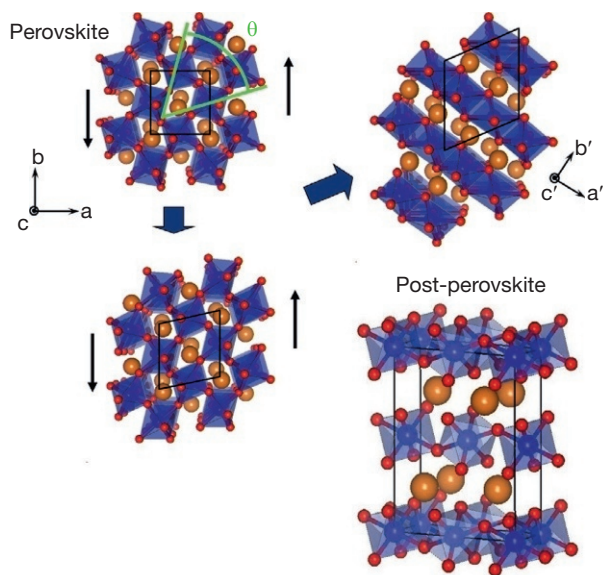


Figure 2 Structural relation between perovskite and post-perovskite under a shear deformation ε_6 (Tsuchiya et al., 2004a,b). This relationship corresponds to the distortion associated with a nucleation center of the post-perovskite transition (Oganov et al., 2005).

relatively high transition pressure is consistent with the earlier observation that the Pt scale predicts much higher pressure than the Au scale in this pressure range at 300 K (Akahama et al., 2002). On the other hand, Hirose et al. (2006a) demonstrated that the transition boundary is located at much lower pressure, 113 ± 2 GPa at 2400 K, when using the Au scale proposed by Tsuchiya (2003). Note that the Tsuchiya (2003)

Au EoS predicts lower pressure by 6 GPa than the MgO scale (Hirose et al., 2008a), which accounts for discrepancy with the results by Tateno et al. (2009) using the MgO scale.

As far as computations are concerned, the basic theoretical framework for these calculations, DFT, is in principle exact. However, this is a one-electron approach and, in practice, approximations for the electronic exchange–correlation energy

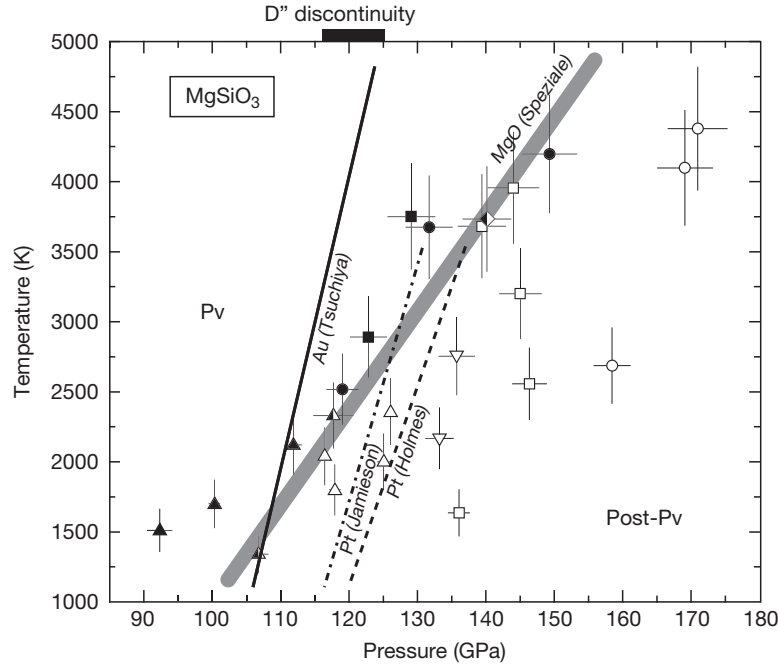


Figure 3 Post-perovskite phase transition boundary in MgSiO_3 determined by high-pressure experiments (Tateno et al., 2009) based on MgO pressure scale (Speziale et al., 2001). Other experimental results by Hirose et al. (2006), Murakami et al. (2004), and Ono and Oganov (2005) are also shown, which used Au scale proposed by Tsuchiya (2003), Pt scales by Jamieson et al. (1982) and Holmes et al. (1989), respectively.

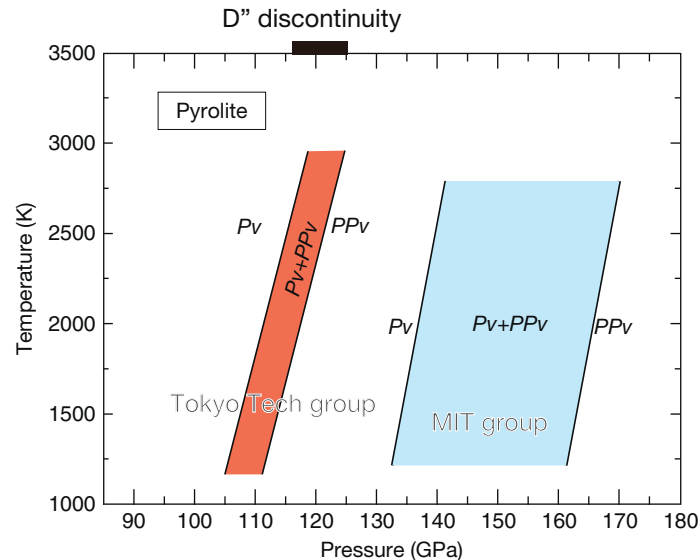


Figure 4 Post-perovskite phase transition boundary in a natural pyrolitic mantle determined by Tokyo Tech group (Murakami et al., 2005; Ohta et al., 2008a) (orange) and by MIT group (Grocholski et al., 2012) (blue). The former studies showed that the transition pressure matches the depth of the D'' discontinuity, but the latter reported much higher transition pressure.

must be made. Among these, the local-density approximation (LDA) (Perdew and Zunger, 1981) and the generalized gradient approximations (GGAs) (Perdew et al., 1996) are the most popular and best tested. The second issue is the computation of free energy associated with atomic motion – quantum at low and classical at high temperatures. Two distinct approximations exist for these limits: The quasi-harmonic approximation (QHA) for low-temperature calculations (Wallace, 1972) assumes atomic vibrations are harmonic, the harmonic potential is only volume-dependent, and vibrational modes do not interact. This approximation proved to be extremely good for several mantle minerals, including MgSiO_3 perovskite and post-perovskite (Wentzcovitch et al., 2010). However, vibrations can be quite anharmonic at high temperatures near melting and atomic motion is essentially classical. In this limit, the method of choice is MD with one caveat – the number of atoms used in simulations needs to be large, $\sim 10^4$, for converged free energy results (Belonoshko et al., 2005). This is in practice beyond the capability of DFT-based calculations and MD with considerably smaller number of atoms is the norm (e.g., Oganov et al., 2001; Zhang et al., 2013). Near phase transitions, anharmonicity may also be very important and quantum in nature. This can complicate greatly the calculation and strategies are still being sought for this case (Zhang et al., 2013). Fortunately, at relevant conditions, MgSiO_3 perovskite and post-perovskite seem to lie well within the range of validity of the QHA (Carrier et al., 2007; Tsuchiya et al., 2005a). Therefore, the QHA has been used in conjunction with vibrational frequencies calculated using density functional perturbation theory to compute free energies of perovskite and post-perovskite. The resulting phase boundary is displayed in Figure 5. The calculated Clapeyron slope of this transition, 7.5 MPa K^{-1} , differs somewhat from measurements (see Table 1), and the deviation seems to be larger than the uncertainty caused by the use of different exchange–correlation functionals, that is, LDA (Perdew and Zunger, 1981) or GGA (Perdew et al., 1996). Anharmonic effects on this phase boundary may be important (Zhang et al., 2013) but have not been investigated yet. Although the phase boundary uncertainty is large, this transition is plausibly associated with the D'' discontinuity at $\sim 125 \text{ GPa}$.

2.05.2.2.2 Post-perovskite phase boundary in peridotitic mantle

The post-perovskite phase transition has been observed not only in pure MgSiO_3 but also in natural compositions such as peridotitic mantle and MORB materials. Murakami et al. (2005) first reported the post-perovskite phase transition in ‘pyrolite’ (KLB-1 peridotite) above 113 GPa and 2500 K based on the Au scale by Tsuchiya (2003), which is recalculated to 120 GPa when using Speziale et al.’s (2001) MgO scale and thus similar to the transition pressure in pure MgSiO_3 (Figure 4). Following up their experiments, Ohta et al. (2008a) augmented the data and demonstrated that the transition occurs between 116 and 121 GPa at 2500 K using the Au scale by Hirose et al. (2008a) that was made on the basis of the Speziale et al.’s MgO scale.

Ono and Oganov (2005) performed similar XRD measurements to determine the phase transition boundary in KLB-1 peridotite. Their results showed that the transition took place at 124 GPa and 2500 K based on the Au scale proposed by Jamieson et al. (1982), which is equivalent to 134 GPa if we

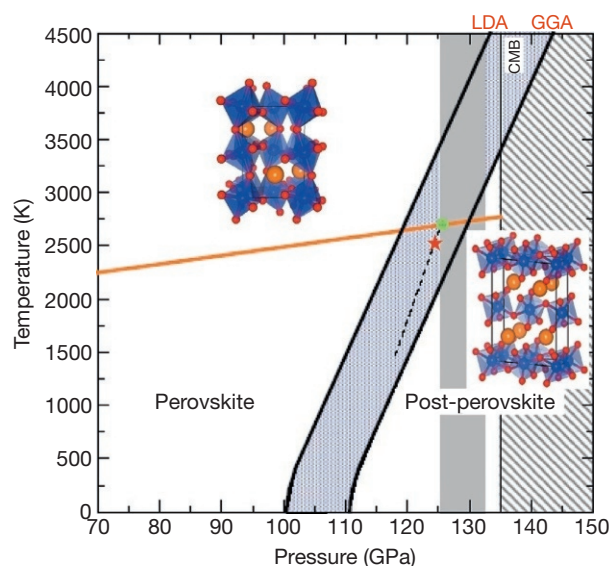


Figure 5 Post-perovskite phase boundary calculated using the local-density approximation (LDA) and generalized gradient approximation. The width of the stripe displays the typical uncertainty associated with the approximations to exchange–correlations energy of the electrons (from Tsuchiya et al., 2004a). The dashed line is the phase boundary proposed by combining experimental transition data (red star) (Murakami et al., 2004) and the Clapeyron slope used to explain the D'' topography by a solid–solid phase change (Sidorin et al., 1999). The vertical gray bar corresponds to the pressure range across the D'' topography. The orange line corresponds to the mantle adiabat (Brown and Shankland, 1981).

Table 1 The Clapeyron slope of the MgSiO_3 post-perovskite phase transition

	Clapeyron slope (MPa K^{-1})	Source
Wu et al.’s scale (2008)	9.7	Hirose et al. (2006a)
Speziale et al.’s scale (2001)	11.5	Hirose et al. (2006a)
Tsuchiya (2004)	5.0	Hirose et al. (2006a)
Holmes et al.’s Pt scale (1989)	7.0	Ono and Oganov (2005)
Jamieson et al.’s Au scale (1982)	8.0	Ono and Oganov (2005)
Theory	7.5, ^a 9.85 ^b	

^aTsuchiya et al. (2004a,b).

^bOganov and Ono (2004).

use Speziale et al.’s MgO scale. Furthermore, recent experiments by Grocholski et al. (2012) reported the transition as between 140 and 169 GPa at 2500 K by Tsuchiya’s (2003) Au scale, (Figure 4) which is converted into 146 and 175 GPa using the MgO scale.

These indicate that the post-perovskite transition pressure estimates in natural peridotite compositions determined by earlier DAC experiments differ by more than 20 GPa (Figure 4). Indeed, the pressure range of the phase transition in a natural peridotite composition (140–169 GPa) reported by Grocholski et al. (2012) is much higher than 112–140 GPa in $(\text{Mg}_{0.9}\text{Fe}_{0.1})(\text{Al}_{0.1}\text{Si}_{0.9})\text{O}_3$ determined by the same group

(Catalli et al., 2009). The main difference between the natural peridotite and $(\text{Mg}_{0.9}\text{Fe}_{0.1})(\text{Al}_{0.1}\text{Si}_{0.9})\text{O}_3$ bulk compositions is the presence of ferropericlase, which narrows the width (pressure range) of the transition but does not increase the average transition pressure (Sinmyo et al., 2011). The origin of inconsistency between Catalli et al. (2009) and Grocholski et al. (2012) is not clear.

One possible source of discrepancy between the previous experimental results is kinetic hindering of the post-perovskite phase transition. Ono and Oganov (2005) repeated a number of heating cycles with changing P - T condition for a given sample to evaluate the growth/reduction of diffraction peaks of perovskite and post-perovskite. However, the transition may have been kinetically hindered in their experiments because phase transitions are commonly sluggish after a high-pressure phase is formed in the first heating cycle (Hirose et al., 2006b). Grocholski et al. (2012) also heated a specific sample repeatedly with changing P - T conditions although the data obtained in the first heating cycle alone defined the relatively high-pressure condition of the phase transition.

Another source of discrepancy is thermal diffusion, often called Soret diffusion, during laser heating. The temperature gradient in a laser-heated sample is relatively large, typically $\pm 10\%$, such that iron migrates to the low-temperature part of the sample (Sinmyo and Hirose, 2010). The long heating duration in laser-heated DAC experiments does not necessarily attain chemical equilibrium (sample grain size is usually limited only to 100 nm and thus long heating duration is not required for equilibrium) but often causes depletion in iron at the hot spot in particular when the sample is mixed with a metal powder of laser absorber (Sinmyo and Hirose, 2010).

Discrepancies in predicted post-perovskite phase transition characteristics are found not only in the average transition pressure but also in the pressure interval of the phase transition (pressure range for coexistence of perovskite and post-perovskite). Experiments by Ono and Oganov (2005) showed a pressure width of less than 3 GPa, corresponding to <50 km depth interval in the deep mantle. Ohta et al. (2008a) demonstrated a pressure width of 5 GPa that corresponds to a depth interval of 90 km. These are slightly broader but generally consistent with the possible sharpness of the D'' discontinuity; seismology has inferred a depth extent of velocity increase up to 50–75 km (Lay, 2008; Revenaugh and Jordan, 1991; Weber et al., 1996) or less than 30 km (Lay and Young, 1989). Note that prediction of too wide of a two-phase domain may in part be due to the errors in pressure determinations in the experiments. On the other hand, a similar discrepancy between seismic observations and experiments has been found for the 410 km seismic discontinuity. The effective depth extent of the seismological expression of the olivine to β -spinel transition may be less than half of the two-phase coexistence region (Stixrude, 1997); possibly, this is also true for the post-perovskite phase transition.

More problematic is the Grocholski et al. (2012) estimation that the post-perovskite transition occurred over a pressure interval of about 25 GPa, much broader than observed by Ono and Oganov (2005) and Ohta et al. (2008a), and incompatible with the existence of a broadband seismic reflecting boundary. Previously, Catalli et al. (2009) and Andraut et al. (2010) also found that the width of the perovskite–post-perovskite two-phase coexistence region is larger than 20 GPa

in Al-bearing $(\text{Mg,Fe})\text{SiO}_3$ bulk composition. Nevertheless, Sinmyo et al. (2011) argued that the iron content in post-perovskite reduces from that of perovskite in the presence of $(\text{Mg,Fe})\text{O}$ ferropericlase, which acts to sharpen the transition. As a result, Grocholski et al. (2012) suggested that Al is key for both deepening and broadening the post-perovskite phase transition, but previous experiments and calculations showed that the effect of 4 wt% Al_2O_3 is not large enough to explain the results of Grocholski et al. (2012) (Akber-Knutson et al., 2005; Tatenko et al., 2005; Tsuchiya and Tsuchiya, 2008). The XRD patterns by Grocholski et al. (2012) include peaks from nitrogen, which was possibly contaminated during cryogenic loading. This might be the source of the discrepancy although the effect of nitrogen is not known. If the phase transition is too gradual to produce a seismic reflection and only is manifested in a gradual velocity increase with depth, it is much harder to uniquely demonstrate the existence of post-perovskite phase in the mantle.

Surely, mantle mineralogy in the deep mantle is likely to be complex, and transition pressures and intervals can be quite sensitive to composition, mineralogy, temperature, etc. Thermodynamic equilibrium calculations in aggregates containing iron- and aluminum-bearing solid solutions, including strong electronic correlation, with spin crossover in ferric iron, and coexisting with ferropericlase, also undergoing spin crossover in ferrous iron, complicate tremendously the problem. Progress is steady though, but thermodynamic modeling needs to be aided by experimental data to give confidence in the calculations.

2.05.2.2.3 Compositional effects

Since the lowermost mantle is a mantle convection boundary layer, it is likely to be chemically heterogeneous due to the accumulation of dense materials. Such dense materials may include subducted MORB crust (Hirose et al., 2005a; Nakagawa and Tackley, 2005; Ricolleau et al., 2010), proto-crust formed and subducted in the early Earth (Boyet and Carlson, 2005; Tolstikhin and Hofmann, 2005), banded iron formation (Dobson and Brodholt, 2005), and products of late-stage crystallization from a basal magma ocean (Labrosse et al., 2007). Such chemical heterogeneity may produce seismic velocity structures including rapid velocity increases and decreases and large-scale lateral variations that make it difficult to identify any phase transition effects, particularly since chemical variations can affect the transition pressure and relative P- and S-wave velocity changes.

The post-perovskite phase transition has been experimentally observed for MORB materials. Combining with Hirose et al. (2005a), the experiments by Ohta et al. (2008a) reported that the transition occurred between 112 and 117 GPa at 2500 K using the Au pressure scale proposed by Hirose et al. (2008a), which was based on and therefore equivalent to the MgO scale. Similar experiments by Grocholski et al. (2012) also demonstrated that MORB underwent transition to post-perovskite between 108 and 122 GPa, broadly consistent with Ohta et al. (2008a). The transition pressure in MORB is lower than that in a peridotitic mantle by at least 4 GPa. It is also noted that MORB includes large amounts ($\sim 25\%$) of silica phase unlike peridotitic mantle material, and the silica phase undergoes structural transition from CaCl_2 type to $\alpha\text{-PbO}_2$ structure in a similar pressure range (Grocholski et al., 2012; Hirose et al., 2005a), resulting in a shear-wave velocity decrease (Karki et al., 1997).

A seismologically observed shear-wave velocity reduction at 2530 km depth (Ohta et al., 2008a) and at 2550–2750 km depth (Konishi et al., 2009) has been attributed to these phase transitions occurring in chemically distinct mantle regions identified as large low shear velocity provinces (LLSVPs) that may have accumulated MORB material.

Detailed compositional effects on the post-perovskite phase transition have been extensively studied. All experimental and theoretical studies except Tsuchiya and Tsuchiya (2008) indicate that the addition of Al stabilizes perovskite at higher pressure relative to post-perovskite (Akber-Knutson et al., 2005; Caracas and Cohen, 2005; Tateno et al., 2005). Experiments by Tateno et al. (2005) showed that the transition starts at 140 GPa at 2500 K in $\text{MgSiO}_3 + 25 \text{ mol\% Al}_2\text{O}_3$ and the pressure interval of transition may be as large as 30 GPa. This suggests that $\sim 5 \text{ mol\% Al}_2\text{O}_3$ in both perovskite and post-perovskite in a pyrolytic lower mantle may increase the initiation of the post-perovskite phase transition by 3 GPa and the pressure interval by 6 GPa compared to pure MgSiO_3 . The calculations by Akber-Knutson et al. (2005) also suggested that the transition occurs between 127 and 140 GPa at 2500 K in $\text{MgSiO}_3 + 6.25 \text{ mol\% Al}_2\text{O}_3$.

On the other hand, the effect of iron has been controversial. Experiments performed by Mao et al. (2004) demonstrated that the post-perovskite phase transition occurred in (Mg,Fe) SiO_3 around 110 GPa, which is much lower than the 125 GPa determined for pure MgSiO_3 by Murakami et al. (2004). More recently, Dorfman et al. (2012) showed that post-perovskite started to form in $(\text{Mg}_{0.61}\text{Fe}_{0.38}\text{Ca}_{0.01})\text{SiO}_3$ bulk composition at 87 GPa and 2150 K. These experimental results are supported by theory, which predicts that the post-perovskite structure is stable with respect to perovskite in FeSiO_3 end-member at all pressures in the Earth's mantle (e.g., Caracas and Cohen, 2005; Stackhouse et al., 2006). Contrary to these experimental and theoretical studies, Murakami et al. (2005) showed that Mg-perovskite is more iron-rich than post-perovskite in a natural pyrolite bulk composition, suggesting that iron stabilizes perovskite relative to post-perovskite. This is reinforced by the later phase transition study on (Mg,Fe) SiO_3 perovskite by Tateno et al. (2007) and the TEM studies by Hirose et al. (2008a,b) and Sinmyo et al. (2011).

2.05.2.2.4 Clapeyron slope of the phase transition boundary

The high positive Clapeyron slope of the post-perovskite phase transition was first estimated by theoretical calculations, although an unspecified solid–solid transition in the deep lower mantle with the slope of $+6 \text{ MPa K}^{-1}$ had been proposed to explain seismological detection of depth variations of the D'' discontinuity before the discovery of post-perovskite (Sidorin et al., 1999). Tsuchiya et al. (2004b) calculated the phase transition boundary at high temperatures, estimating a Clapeyron slope of $+7.5 \text{ MPa K}^{-1}$. A slightly larger (about $+10 \text{ MPa K}^{-1}$) slope was predicted by Oganov and Ono (2004).

High-pressure DAC experiments also indicate a large positive value of the Clapeyron slope for the post-perovskite phase transition in pure MgSiO_3 , although the results are strongly dependent on the pressure scale. Ono and Oganov (2005) estimated $+7 \text{ MPa K}^{-1}$ based on the Holmes et al. (1989) Pt pressure scale. Hirose et al. (2006a) reported $+5 \text{ MPa K}^{-1}$ using Tsuchiya's Au scale and $+11 \text{ MPa K}^{-1}$ with Speziale et al.'s MgO scale. More recent study by Tateno et al. (2009) based on

experiments over much wider P – T range gave $+13 \text{ MPa K}^{-1}$ based on the MgO scale. Similar high positive Clapeyron slope is also found in post-perovskite phase transition in analog material such as CaIrO_3 ($+17 \text{ MPa K}^{-1}$) (Hirose and Fujita, 2005).

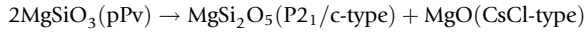
A special thermal EoS for MgO was engineered with accuracy of few GPa up to $\sim 5000 \text{ K}$ and 400 GPa to reinterpret data on the post-perovskite transition boundary (Wu et al., 2008). It combined consistently DAC data, ultrasound velocity data, and first-principles results. The experimental post-perovskite phase boundary obtained using this EoS gave a Clapeyron slope more consistent with those obtained by first-principles calculations (Oganov and Ono, 2004; Tsuchiya et al., 2004a,b) (see Table 1). It also supported the idea that the post-perovskite phase transforms back to perovskite in a high temperature gradient just above the CMB (Hernlund et al., 2005).

The determination of the Clapeyron slope for a natural mantle composition is more difficult than for pure MgSiO_3 , because the transition (1) occurs over some pressure range and (2) is more sluggish in a multicomponent system. Experiments performed by Ohta et al. (2008a) did not tightly constrain but best estimated the Clapeyron slope in a pyrolytic mantle to be $+8 \pm 4 \text{ MPa K}^{-1}$. Grocholski et al. (2012) estimated $+5.6 \pm 0.8 \text{ MPa K}^{-1}$ based on Tsuchiya's Au scale, which is very similar to the $+5 \text{ MPa K}^{-1}$ for pure MgSiO_3 using the same pressure scale (Hirose et al., 2006a) and therefore likely corresponds to $\sim +11 \text{ MPa K}^{-1}$ with the MgO scale. These results suggest that the Clapeyron slope of post-perovskite phase transition in a natural mantle composition is similar to that in MgSiO_3 and may be as high as 11 – 13 MPa K^{-1} . Given the likelihood of substantial lateral variations in temperature in the D'' thermal boundary layer, there are likely to be substantial depth variations in the phase boundary and any associated seismic velocity changes.

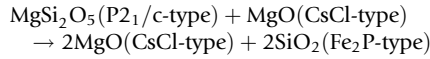
2.05.2.2.5 The stability of MgSiO_3 post-perovskite at extreme pressures

The stability of the post-perovskite phase with increasing pressure is important for understanding the internal structure and dynamics of large rocky planets – super-Earth-type exoplanets – which should be relatively abundant and may exist around as many as 23% of stars (Howard et al., 2010). Early studies focused on the internal structure of these planets and on the viability of plate tectonics (Seager et al., 2007; Sotin et al., 2007; Valencia et al., 2006, 2007a,b,c). More recent dynamical modeling studies have included some depth-dependent properties (Tackley et al., 2013), but not the effect of deeper phase transitions, which were considered by van den Berg et al. (2010b). Views on the 'next' phase transition in MgSiO_3 , the post–post-perovskite transition, are still evolving but the trend toward full dissociation into elementary oxides, MgO and SiO_2 (Umemoto et al., 2006a,b), is unaltered. It just seems that the dissociation process is gradual, not direct. MgSiO_3 post-perovskite was first predicted to dissociate into CsCl-type MgO and cotunnite-type SiO_2 at $\sim 11 \text{ Mbar}$ (Umemoto et al., 2006b). This prediction was slightly revised after the identification of another polymorph of SiO_2 , the Fe_2P -type phase (Tsuchiya and Tsuchiya, 2011; Wu et al., 2011), with the latter being stable at low temperatures but transforming to the cotunnite-type phase at $\sim 6000 \text{ K}$. A more gradual dissociation process was later identified (Umemoto

and Wentzcovitch, 2011). The two-stage dissociation pathway consists in the gradual exsolution of MgO from MgSiO₃

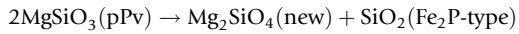


at ~9 Mbar, followed by full dissociation of MgSi₂O₅



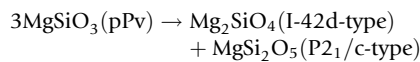
at ~21 Mbar. The new P2₁/c-type MgSi₂O₅ phase was identified by following dynamical instabilities in MgSi₂O₅ in the structure of CaGe₂O₅ with space group *Pham* (Nemeth et al., 2007), a post-titanate-type phase. This phase has 32 atoms per cell, and it has two types of silicon, one ninefold- and eightfold-coordinated, while magnesium is ninefold-coordinated.

This finding raised even more questions about the dissociation process. Could, alternatively, SiO₂ also exsolve gradually? A possible exsolution mechanism is

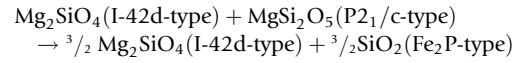


An adaptive genetic algorithm was developed used to search for stable structures with composition Mg₂SiO₄ and to repeat the search for structures with composition MgSi₂O₅ (Wu et al., 2014). This search confirmed the stability of the P2₁/c-type MgSi₂O₅ phase and identified a new high-pressure form of Mg₂SiO₄. This structure is body-centered tetragonal with space group I-42d. The cation configuration of this phase is identical to that of Zn₂SiO₄-II whose space group is I-42d also (Marumo and Syono, 1971). The difference between I-42d-type Mg₂SiO₄ and Zn₂SiO₄-II is in the oxygen arrangement. Mg₂SiO₄ is much more closely packed than Zn₂SiO₄-II. Both Mg and Si atoms in Mg₂SiO₄ are eightfold-coordinated, while Zn and Si atoms in Zn₂SiO₄-II are fourfold (tetrahedrally)-coordinated. The crystal structures of I-42d-type Mg₂SiO₄ and P2₁/c-type MgSi₂O₅ together with the corresponding local structures are shown in Figure 6.

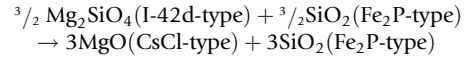
This enlarged composition space of possible structures now reveals a more complex three-step dissociation process – MgSiO₃ post-perovskite first decomposes into two phases at 7.7 Mbar, one rich (poor) and one poor (rich) in SiO₂ (MgO):



In the presence of Mg₂SiO₄, MgSi₂O₅ breaks down into Mg₂SiO₄ and SiO₂ at 12.5 Mbar:



The complete dissociation into oxides then takes place at ~30.9 Mbar:



This sequence of transitions is shown in Figure 6. The dissociation starts at 8 Mbar and is completed at ~31 Mbar. This pressure range is expected to change somewhat at high temperatures though. This prediction contrasts with the direct dissociation previously predicted at ~11 Mbar (Umemoto et al., 2006b) and the two-step exsolution of MgO predicted between ~9 and 21 Mbar (Umemoto and Wentzcovitch, 2011). Among this latest sequence of dissociation transitions, only the first two are relevant for understanding the mantle of terrestrial exoplanets with up to 10 Earth masses. Mantle pressures in these planets are expected to reach ~14 Mbar and temperatures ~6,000 K (Sotin et al., 2007). In overall, these results suggest that more complex sequences of phase transitions could be found by considering intermediate phases with different compositions. The large ionic (LDA) gaps of at least 5 eV found in all phases suggest that phases with different molar fractions of MgO and SiO₂ with even more complex structures are the most natural candidates for future investigations.

2.05.3 D'' Region and Evidence for Post-Perovskite

Seismological observations have long indicated a relatively simple structure of the lower mantle with smooth P- and S-wave velocity and density increases with depth from the transition zone down to the much more heterogeneous D'' region (see 'Deep Earth Structure'). In the lowermost 300–500 km of the mantle, seismic wave travel times and waveforms indicate reductions in radial velocity gradients, abrupt increases and decreases in velocity, increases in short-period wave scattering, increase in anisotropic properties, and strong lateral gradients in structure. The D'' region has a preponderance of large-scale (degree-2 and degree-3) variations, with two LLSVPs extending upward several hundred kilometers from the CMB beneath the southern Pacific and Africa and high P- and S-wave velocities below the circum-Pacific subduction zones. Strong S-wave and intermittent P-wave velocity increases 100–300 km above the CMB have

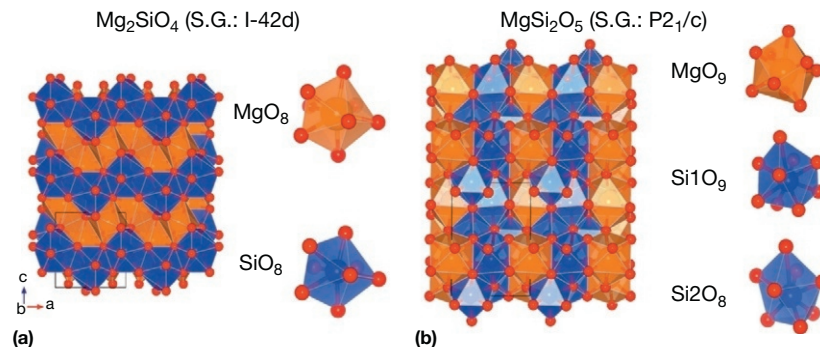


Figure 6 Crystal structures of I-42d Mg₂SiO₄ and P2₁/c MgSi₂O₅.

been observed primarily in the high-velocity regions, which are generally thought to have lower than average temperatures due to the downwelling of oceanic lithosphere. A widely observed strong S-wave velocity increase of 2–3% several hundred kilometers above the CMB is often designated the D'' discontinuity. It was more than 20 years after its initial observation by Lay and Helmberger (1983) that the post-perovskite phase transition first provided a possible explanation for this structure. The expectation that perovskite-to-post-perovskite transition will occur at lower pressure for lower temperatures suggests that any associated seismological signature should be found at shallower depth in higher-velocity regions. The seismological structures detected in the lowermost mantle require both thermal and chemical heterogeneities and dynamical processes that sustain the complexity. The consideration of possible manifestations of deep mantle post-perovskite must allow for significant variations in temperature and composition (Lay and Garnero, 2007).

2.05.3.1 Elasticity

The post-perovskite transition in MgSiO_3 at conditions similar to those expected at the D'' discontinuity offers a candidate framework for interpreting the properties of this region. However, the complexity of the D'' region and the uncertain local mineral composition raise questions about its geophysical significance. The contrast between the elastic properties of perovskite and post-perovskite is critical to establishing the presence of post-perovskite in this region. In particular, one would like to verify whether (i) shear and longitudinal velocity changes across the D'' discontinuity and (ii) the anticorrelation between shear and bulk velocity heterogeneities in this region can be better understood by invoking the post-perovskite transition.

The elasticity of perovskite and post-perovskite phases has been calculated by first principles using two complementary techniques: MD (Oganov et al., 2001; Stackhouse and Brodholt, 2007) and QHA in conjunction with phonon frequencies (Wentzcovitch et al., 2004, 2009). The QHA method offers detailed information in a continuum in pressure and temperature parameter space and is very useful to compute pressure and temperature gradients and lateral heterogeneities in great detail.

The elastic coefficients of MgSiO_3 post-perovskite are remarkably different from those of perovskite (see Figure 7). Post-perovskite is a layered structure, expands more anisotropically, and has more complex pressure- and temperature-dependent elastic behavior than perovskite (Tsuchiya et al., 2004b). However, its aggregate moduli do not differ dramatically from those of perovskite. The adiabatic bulk moduli of both phases, K (Figure 8), are similar at $P > 80$ GPa. This is also true for other thermodynamic properties (Tsuchiya et al., 2005a). The shear modulus, G , of post-perovskite is larger and has larger pressure and temperature gradients at deep lower mantle conditions. Considering that post-perovskite is $\sim 1.5\%$ denser than perovskite at D'' conditions, the resulting effect on velocities are easy to rationalize (see Figure 9). Because of G , post-perovskite's V_S is larger and has larger pressure and temperature gradients. The longitudinal velocity, V_P , is a little larger and has slightly larger gradients because of G as well (see Figure 9). In contrast, the bulk velocity, V_Φ , is a smaller than that of perovskite because of their similar K and

the larger density (ρ) of post-perovskite. Although minor differences remain, these results are in general agreement with those based on first-principles MD (Oganov et al., 2001; Stackhouse and Brodholt, 2007).

2.05.3.2 Velocity Jumps and Lateral Heterogeneity

These predicted contrasts between perovskite and post-perovskite velocities manifest across the phase transitions as a positive jump in V_S , negative jump in V_Φ , and small positive jump in V_P (see Figure 10) (Wentzcovitch et al., 2006; Wookey et al., 2005). These results are consistent with seismic velocity jumps observed 200–300 km above the core–mantle boundary in certain places but most easily detected beneath regions of past subduction, presumably cold places, such as beneath Central America (e.g., Hutko et al., 2008, 2009; Lay and Helmberger, 1983). There, $\Delta V_S > \Delta V_P$ and $\Delta V_S \sim 2\text{--}3\%$ are observed, but this observation is clearly a regional property of a notably heterogeneous layer (Garnero, 2004; Lay and Garnero, 2004; Lay et al., 1998b, 2004; Wyssession et al., 1998).

A well-known property of D'' revealed by early global tomography models (e.g., Masters et al., 2000) is anticorrelation between large-scale lateral V_Φ and V_S heterogeneities. The likely cause(s) of heterogeneities is best addressed by comparing simultaneously the magnitude of average heterogeneity ratios such as $R_{S/P} = (\partial \ln V_S / \partial \ln V_P)_P$ and $R_{\Phi/S} = (\partial \ln V_\Phi / \partial \ln V_S)_P$, to computational predictions or experimental measurements at relevant conditions (Karato and Karki, 2001). It is known that in the shallow lower mantle, $R_{S/P} \sim 2.3$ and $R_{\Phi/S} \sim 0.0$, whereas in D'', $R_{S/P} \sim 3.4$ and $R_{\Phi/S} \sim -0.2$ (Masters et al., 2000). Heterogeneity ratios produced by isobaric temperature changes in pure post-perovskite and perovskite aggregates are displayed in Figure 11(a) and 11(b) along with the seismic parameters extracted from Masters et al. (2000) and reported by Karato and Karki (2001). In pure perovskite aggregates, $R_{S/P}$ increases with pressure and temperature but reaches at most 2.3 at 135 GPa and 4000 K (Figure 11(b)), whereas $R_{\Phi/S}$ is approximately pressure-independent and slightly decreases with temperature to reach 0.16 at the same conditions (see Figure 12(b)). In post-perovskite, $R_{S/P}$ decreases with pressure, but because of its larger $(\partial G / \partial T)_P$, it increases more rapidly with temperature to reach ~ 2.5 at the same conditions (Figure 11(a)). $R_{\Phi/S}$ is smaller for post-perovskite, 0.1, at these conditions (see Figure 12(a)). It has been argued that anelasticity, anisotropy, and lateral variations in calcium content in the deepest mantle might be necessary to produce large values for $R_{S/P}$ and negative values for $R_{\Phi/S}$, unless there is a phase transformation (Karato and Karki, 2001).

Figures 11(c) and 12(c) compare these heterogeneity ratios caused by the post-perovskite transition along the calculated phase boundary (Figure 5). $R_{S/P} > 6$ and $R_{\Phi/S} < -0.5$ results from this phase change. This indicates that lateral variation in post-perovskite abundance can enhance these seismic parameters as observed. This effect was estimated by Oganov and Ono (2004) assuming the temperature dependences of perovskite and post-perovskite velocities were the same. Coexisting secondary phases such as ferropericlase and CaSiO_3 perovskite will decrease these anomaly ratios. Besides, the post-perovskite

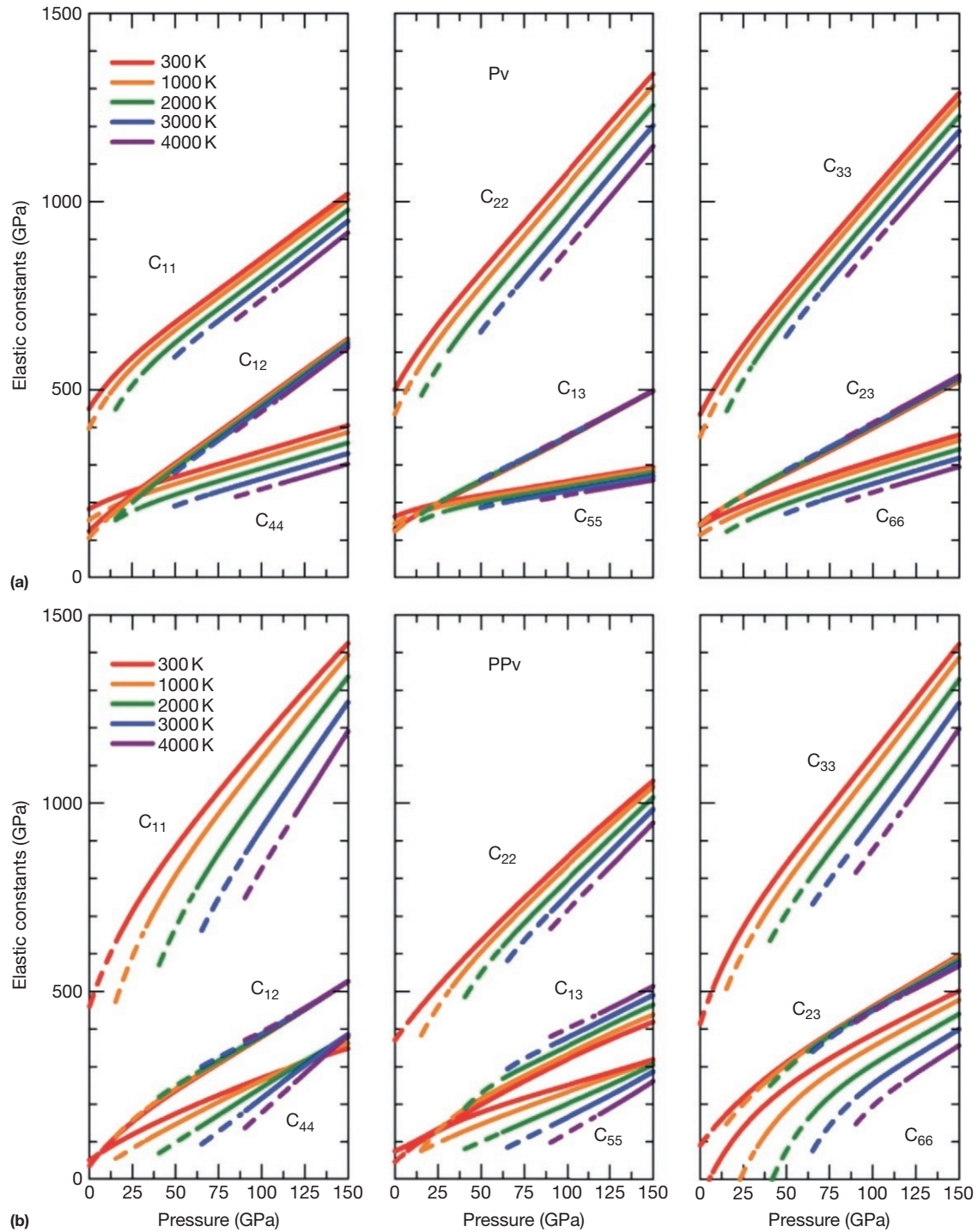


Figure 7 Elastic coefficients of (a) perovskite and (b) post-perovskite obtained using LDA. Reproduced from Wentzcovitch RM, Justo JF, Wu Z, da Silva CRS, Yuen D, and Kohlstedt D (2009) Anomalous compressibility of ferropericlasite throughout the iron spin crossover. *Proceedings of the National Academy of Sciences of the United States of America* 106: 8447–8452.

phase transition on solid solutions should open a binary loop that will smooth these velocity contrasts (Grocholski et al., 2012). Nevertheless, the effect of lateral variations in post-perovskite abundance on these seismic parameters seems very robust and indicative of the presence of post-perovskite in the

D'' region, as later supported by the statistical analysis of Trampert et al. (2004).

As pointed out earlier, the topography of D'' is consistent with a solid–solid phase transition with positive Clapeyron slope ($\sim 4\text{--}10 \text{ MP K}^{-1}$) induced by lateral temperature

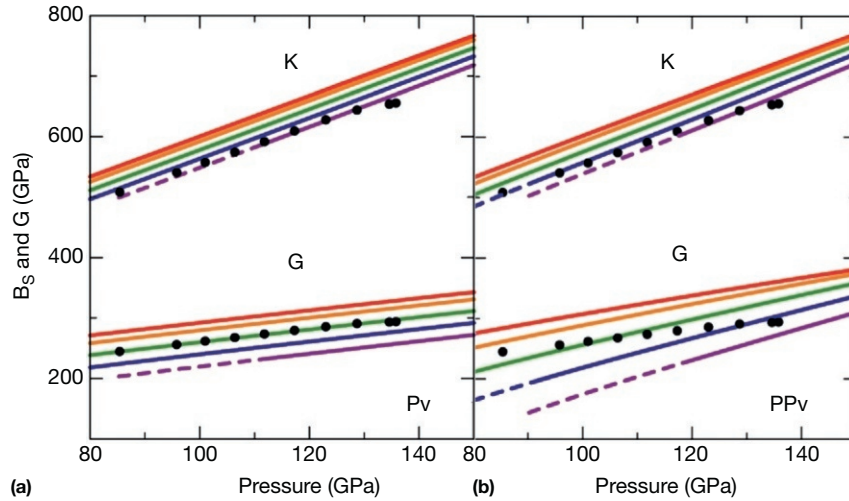


Figure 8 Adiabatic bulk modulus (K) and shear modulus (G) of (a) perovskite and (b) post-perovskite. Same color code as [Figure 7](#) applies.

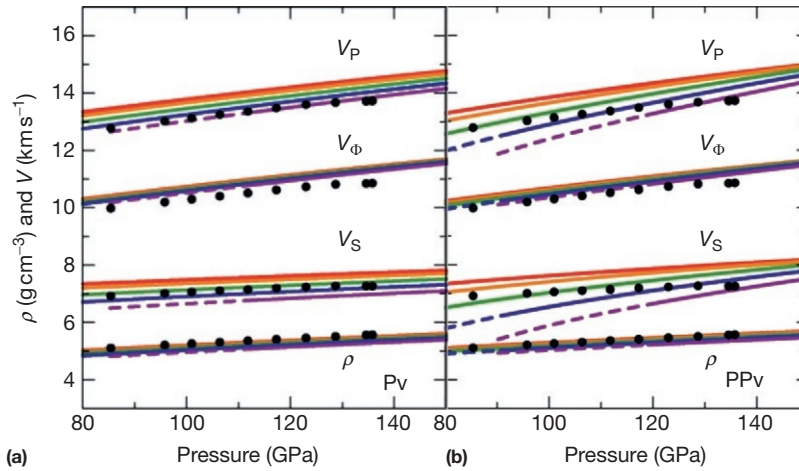


Figure 9 Isotropic longitudinal (V_P), bulk (V_ϕ), and shear (V_S)-wave velocities and density (ρ) of (a) perovskite and (b) post-perovskite. Filled circles in (a) and (b) are PREM values ([Dziewonski and Anderson, 1981](#)) for comparison. Same color code as [Figure 7](#) applies.

variations ([Sidorin et al., 1999](#)). The anticorrelation between V_ϕ and V_S heterogeneities and their geographic locations are also consistent with this assumption if the post-perovskite phase is abundant in the D'' region. Beneath the central Pacific, V_ϕ is faster and V_S is slower than their spherical averages, whereas beneath the circum-Pacific, the opposite is observed. These regions are generally considered to be hotter and colder than average, respectively. The positive Clapeyron slope suggests that hotter regions should contain less post-perovskite and therefore have faster V_ϕ and slower V_S , whereas colder regions should contain more post-perovskite and have slower V_ϕ and faster V_S , as observed. Lateral variations in phase abundances alone do not account for the complex nature and properties of D'' . Nevertheless, this perspective is helpful as a reference starting model to attempt understanding the D'' region. Secondary phases and minor element partitioning on the post-perovskite phase boundary and on aggregate elasticity, particularly the important effect of iron ([Mao et al., 2005](#)), must be addressed first before a more quantitative reference mineralogical model for D'' is developed. The origin of the negative $R_{\phi/S}$ above D'' indicated in [Figure 12](#) is also unclear.

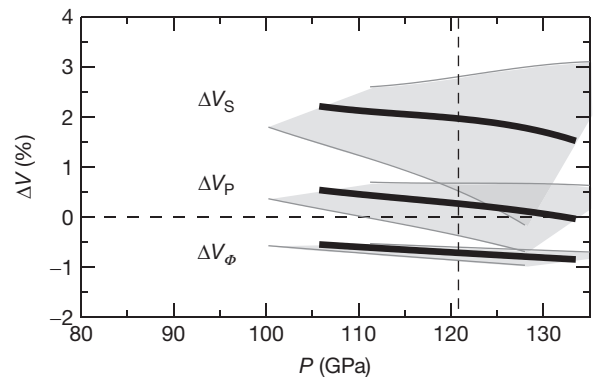


Figure 10 Velocity jumps across the phase boundary shown in [Figure 5](#). Thick black lines represent the jumps at the center of the phase boundary with a density functional theory-related uncertainty of ~ 10 GPa. Shaded areas are possible values throughout the boundary uncertainty domain. Open triangles and squares, respectively, are results from molecular dynamics simulations at 135 GPa and 4000 K and 136 GPa and 3000 K. The vertical dashed line indicates the pressure at approximately the top of the D'' discontinuity.

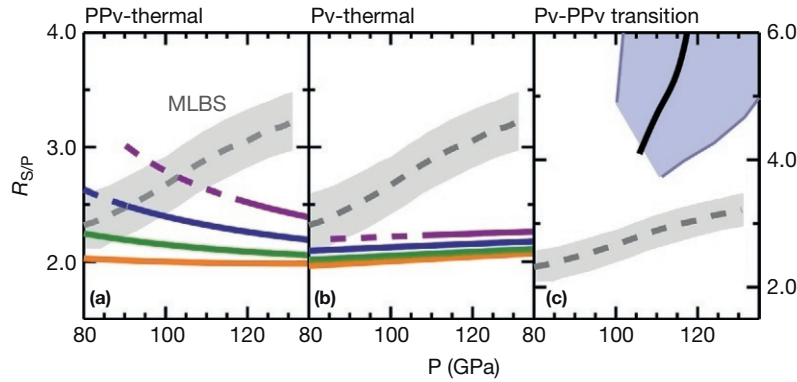


Figure 11 Heterogeneity ratio $R_{S/P} = (\partial \ln V_S / \partial \ln V_P)_P$ caused by lateral temperature variations (a) in perovskite, (b) in post-perovskite, and (c) across the phase boundary. Blue-shaded area in (c) is related with the uncertainty in the post-perovskite phase boundary shown in [Figure 5](#). Seismic values are extracted from [Masters et al. \(2000\)](#).

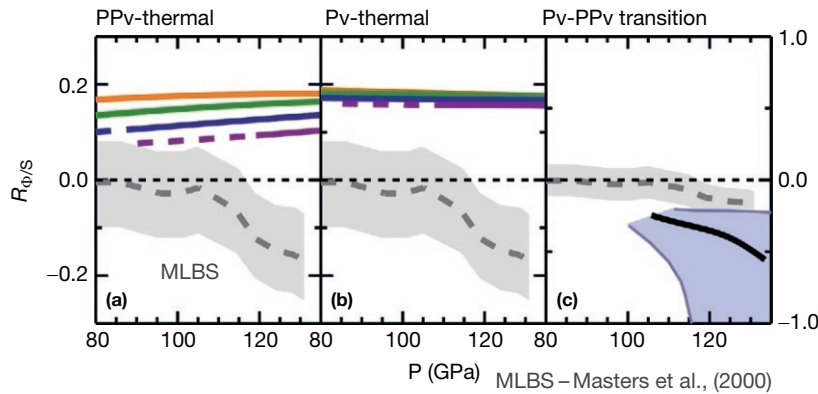


Figure 12 Heterogeneity ratio $R_{\phi/S} = (\partial \ln V_\phi / \partial \ln V_S)_P$ caused by lateral temperature variations (a) in perovskite, (b) in post-perovskite, and (c) across the phase boundary. Shaded areas have the same meaning as in [Figure 11](#).

There is indication that this effect could, for instance, originate in lateral temperature variations in the spin crossover in ferro-periclase ([Wu and Wentzcovitch, 2013](#); [Wu et al., 2013](#)), but the extent to which this can be explained is still not clear.

These results suggest that a third heterogeneity ratio, $R_{\rho/S} = (\partial \ln \rho / \partial \ln V_S)_P$, should be positive for the phase transition and perhaps increase with depth in the lowermost mantle (see lowest portion of [Figure 13](#)), unless other effects or chemical heterogeneities ([Humayun et al., 2004](#); [Karato and Karki, 2001](#); [Lay et al., 2004](#)) occur simultaneously. Some 3D density models do not support this prediction ([Ishii and Tromp, 1999](#)), whereas others do ([Romanowicz, 2001](#)). Estimates of this parameter obtained by joint inversions of seismic and geodynamic data also tend to offer a positive ratio ([Forte et al., 1994](#)). It appears that until a clear consensus on the 3D structure of the density in the mantle is reached, this issue will remain open. Recently, it has been pointed out that an average excess density of 0.4% in the lowermost mantle is admissible within normal mode constraints ([Garnero et al., 2004](#)), in agreement with our expectations.

2.05.3.3 Anisotropy

Significant shear-wave polarization anisotropy has been detected in the lowermost mantle, in particular under the

circum-Pacific regions, where the horizontally polarized S-wave velocity (V_{SH}) is faster by 1–3% than the vertically polarized S-wave velocity (V_{SV}) (e.g., Section 1.19; [Lay et al., 1998a](#); [Panning and Romanowicz, 2004](#)). The overlaying lower mantle appears to have less anisotropic effects on seismic waves, indicating that D'' structure has distinct anisotropic properties. Since single-crystal elastic anisotropy of post-perovskite is strong, such seismic anisotropy is plausibly attributed to the lattice-preferred orientation (LPO) of post-perovskite, although the anisotropy of ferropericlase has been also stressed ([Wentzcovitch et al., 2006](#); [Yamazaki and Karato, 2002](#); [Yamazaki et al., 2009](#)).

The LPO of a mineral depends on its deformation mechanisms, particularly the activated slip systems. For post-perovskite, the layering plane (010) was originally suggested to be a dominant slip plane from crystallographic considerations ([Iitaka et al., 2004](#); [Murakami et al., 2004](#); [Oganov and Ono, 2004](#)). Indeed, the (010) slip plane is supported by the deformation experiments on CaIrO_3 analog ([Miyajima et al., 2006](#); [Niwa et al., 2007](#)). Other slip systems such as (100) or (110) have been also suggested by both theory and experiments on MgSiO_3 and MgGeO_3 ([Merkel et al., 2006, 2007](#); [Oganov et al., 2005](#)). [Walte et al. \(2009\)](#) pointed out that the earlier deformation experiments in a DAC by [Merkel et al. \(2006, 2007\)](#) observed ‘phase transformation texture,’ which is different from ‘deformation texture.’

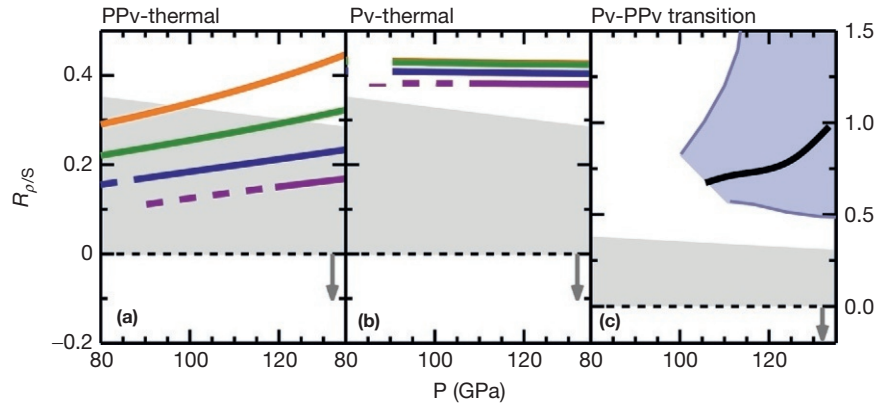


Figure 13 Heterogeneity ratio $R_{\rho/S} = (\partial \ln \rho / \partial \ln V_S)_P$ caused by lateral temperature variations (a) in perovskite, (b) in post-perovskite, and (c) across the phase boundary. Shaded areas have the same meaning as in [Figure 11](#).

More recent experiments by [Okada et al. \(2010\)](#) first demonstrated that (001) is a dominant slip plane of post-perovskite using MgGeO_3 analog. [Miyagi et al. \(2010\)](#) argued that the deformation texture of MgSiO_3 post-perovskite is the same as the transformation texture and concluded that (001) is the slip plane. This is consistent with first-principles results ([Wentzcovitch et al., 2006](#)) (see [Figure 14](#)). [Hirose et al. \(2010\)](#) performed high-temperature deformation experiments on MnGeO_3 post-perovskite and confirmed the (001) slip plane is dominant at lower mantle P - T conditions.

For the (001) slip plane, observed seismic anisotropy can be reconciled with the LPO of post-perovskite, because the perfect alignment of post-perovskite with (001) parallel to the horizontal plane produces 8–15% shear splitting, larger than for any other slip system. The maximum 3% polarization anisotropy observed in the D'' layer can be accounted for by LPO of post-perovskite with less than 25% alignment on the basis of the elastic constants predicted by [Stackhouse and Brodholt \(2007\)](#).

2.05.4 Transport Properties

2.05.4.1 Viscosity

The rheological properties of MgSiO_3 -rich post-perovskite are of importance to the dynamics in the D'' layer. Relevant experiments on the deformation of post-perovskite and on its grain growth rate are difficult to perform at the lowermost mantle high P - T conditions. Thus, extensive experiments using the CaIrO_3 analog have been made at low pressures (<3 GPa).

[Yoshino and Yamazaki \(2007\)](#) examined grain growth kinetics of CaIrO_3 perovskite and post-perovskite aggregates and found that the grain growth of post-perovskite is distinctly slower than that of perovskite. Such sluggish grain growth may be caused by the strongly anisotropic shape of post-perovskite. Grain-size-sensitive diffusion creep is the dominant deformation mechanism of post-perovskite, at least right after the phase transformation in descending slabs, and the initially small grain size may induce significant softening of the D'' layer. The slow growth rate of post-perovskite maintains its small grain size and resulting weakness.

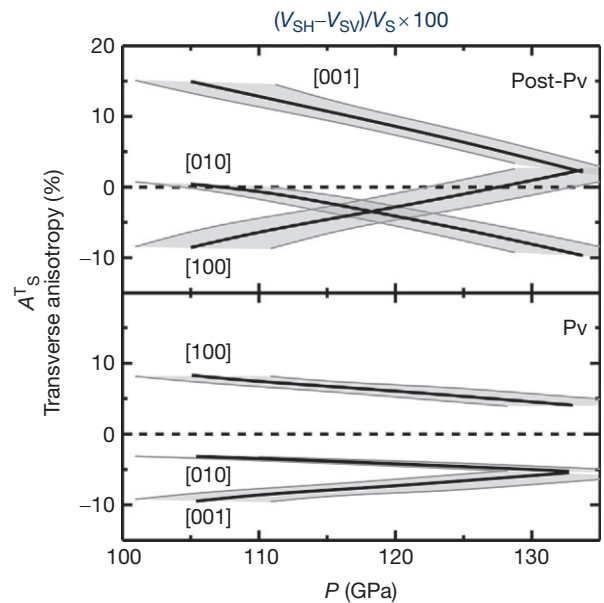


Figure 14 Shear-wave splittings, $(V_{SH} - V_{SV})/V_S$, in MgSiO_3 post-perovskite and perovskite, along the thermodynamic phase boundary shown in [Figure 5](#) with respective uncertainties. These results correspond to horizontally (V_{SH}) and vertically (V_{SV}) polarized shear waves propagating in transversely isotropic aggregates with three possible alignments of the major crystalline axes along the vertical direction.

[Hunt et al. \(2009\)](#) carried out deformation experiments on both perovskite and post-perovskite in the CaIrO_3 system below 3 GPa. Their results demonstrated that post-perovskite is at least five times weaker, and possibly significantly more so, than perovskite. They performed experiments with a grain size sufficiently large to be outside the field of grain-size-sensitive plasticity. This confirms that weakening is not an effect of grain-size reduction.

Theoretical calculations by [Ammann et al. \(2010\)](#) demonstrated that diffusion of Mg^{2+} and Si^{4+} in post-perovskite is extremely anisotropic. Assuming diffusion creep is a dominant deformation mechanism of post-perovskite in the D'' layer, the

fast diffusion direction will render post-perovskite up to four orders of magnitude weaker than perovskite.

These studies suggest strong viscosity contrast between perovskite and post-perovskite. However, the inference of very weak post-perovskite remains debated, with other investigations arguing for a neutrally viscous or even a stronger post-perovskite (Karato, 2011). The rheology of post-perovskite has a first-order influence on mantle dynamics and thermal evolution (Cizkova et al., 2010; Nakagawa and Tackley, 2006; Tosi et al., 2010). If post-perovskite in the mantle is actually very weak, it significantly amplifies the influence relative to that calculated for post-perovskite with neutral viscosity.

2.05.4.2 Thermal Conductivity

The thermal boundary layer at the bottom of the mantle is a region where heat is transported predominantly by conduction from the core into the mantle. Conductive heat is given by the product of temperature gradient and thermal conductivity of the lowermost mantle materials. With known thermal conductivity values, one can estimate heat flow from thermal gradient (see a review by Lay et al., 2008), or vice versa.

Researchers often assume a thermal conductivity, k , of $10 \text{ W m}^{-1} \text{ K}^{-1}$ for the lowermost mantle, based on Stacey (1992). The thermal conductivity is the sum of lattice component and radiative component. The radiative part of the thermal conductivity of perovskite has been measured at high pressure by Goncharov et al. (2008) and Keppler et al. (2008). The former study reported only $\sim 0.5 \text{ W m}^{-1} \text{ K}^{-1}$ at the top of D'' layer and possibly $\sim 1 \text{ W m}^{-1} \text{ K}^{-1}$ at the CMB (radiative thermal conductivity increases with increasing temperature), which is relatively small compared to lattice contribution. On the other hand, the latter experiments demonstrated that the radiative component contributes greater than $5 \text{ W K}^{-1} \text{ m}^{-1}$ at the CMB, suggesting that the conventional value of $10 \text{ W m}^{-1} \text{ K}^{-1}$ underestimates the actual thermal conductivity. The source of inconsistency between these two studies is not clear, and thus, the radiative part of the thermal conductivity for perovskite (and post-perovskite) remains an open question.

For the lattice component of thermal conductivity, Osako and Ito (1991) obtained the conductivity of MgSiO_3 perovskite from the measurements of thermal diffusivity at ambient condition (conductivity is calculated from diffusivity, density, and heat capacity). Both high-pressure measurements and calculations have commenced recently. Manthilake et al. (2011) measured lattice thermal diffusivity of MgSiO_3 -rich perovskite and (Mg,Fe)O ferropericlase up to 26 GPa and 1073 K in a multi-anvil apparatus, the pressure corresponding to the uppermost lower mantle. They also examined the effect of chemical impurity, demonstrating that only 3 mol% Fe and 2 mol% Al in perovskite significantly diminish the diffusivity at 300 K although less at higher temperatures of the lower mantle. Relatively large extrapolation of their measurements provides $k = 8.4 \pm 1.2 \text{ W m}^{-1} \text{ K}^{-1}$ at the CMB, comparable to the conventional value, assuming radiative contribution is small. More recently, Ohta et al. (2012b) measured thermal diffusivity of MgSiO_3 perovskite and post-perovskite up to 144 GPa at room temperature, by applying thermorefectance method in a DAC (Yagi et al., 2011). Considering the value for

ferropericlase and the temperature effect of reducing the conductivity of perovskite from Manthilake et al. (2011), Ohta et al. estimated a lattice conductivity of $11 \text{ W m}^{-1} \text{ K}^{-1}$ at the CMB if perovskite is present there. On the other hand, Ohta et al. (2012b) also found that MgSiO_3 post-perovskite exhibits 60% higher thermal diffusivity than perovskite at equivalent condition, approximately consistent with the measurements of the CaIrO_3 analog that indicate that the thermal conductivity of post-perovskite phase is nearly twice as high as that of perovskite phase (Hunt et al., 2012; Keawprak et al., 2009).

The thermal conductivity of MgO has been calculated at lower mantle P - T conditions in recent studies (de Koker et al., 2012; Haigis et al., 2012; Stackhouse et al., 2010; Tang and Dong, 2010). All such calculations show very high conductivity of MgO, far exceeding the values of perovskite, although the results vary from ~ 80 to $150 \text{ W m}^{-1} \text{ K}^{-1}$ at the CMB. The conductivity of MgSiO_3 perovskite was also calculated by Haigis et al. (2012), predicting $10.8 \text{ W m}^{-1} \text{ K}^{-1}$ for a mixture of MgSiO_3 perovskite + MgO, again consistent with the traditional value. More recent calculations by Dekura et al. (2013) showed somewhat lower value of about $5 \text{ W m}^{-1} \text{ K}^{-1}$ for peridotitic material at the CMB. The calculations by Haigis et al. (2012) also demonstrated that the thermal conductivity MgSiO_3 post-perovskite is $167 \pm 25 \text{ W m}^{-1} \text{ K}^{-1}$ at 135 GPa and 300 K, which is much higher than $65 \pm 14 \text{ W m}^{-1} \text{ K}^{-1}$ measured by Ohta et al. (2012b). Ohta et al. assumed a temperature effect the same as that for perovskite, while Haigis et al. predicted a much larger temperature effect. As a result, the former concluded 60% higher conductivity than perovskite, but the latter suggested very similar conductivity.

These results are summarized in Table 1. If MgSiO_3 -rich perovskite is present right above the CMB, the thermal conductivity of the thermal boundary layer may be 8 – $11 \text{ W m}^{-1} \text{ K}^{-1}$ or higher if radiative conductivity is $\sim 5 \text{ W m}^{-1} \text{ K}^{-1}$. On the other hand, if post-perovskite is the principal mineral in the thermal boundary layer, the conductivity can be much larger, depending on the temperature effect on the conductivity of post-perovskite.

2.05.4.3 Electric Conductivity

Relatively high electric conductivity of the lowermost mantle can cause strong electromagnetic coupling between the solid mantle and liquid core, which may play an important role in modulating the length of a day (rotational speed of the Earth's crust and mantle) (Holme, 1998) and precession of the Earth's rotation axis (Buffett et al., 2000). Enhanced electric conductivity of post-perovskite relative to perovskite was originally suggested by measurements for the CaIrO_3 analog (Ohgushi et al., 2006). This is because electrons are expected to be more conducting within the a - c planes owing to the layered structure of post-perovskite. Ono et al. (2006) considered high electric conductivity of MgSiO_3 -rich post-perovskite in the Earth's lowermost mantle, based on earlier shock-wave measurements of Al_2O_3 with post-perovskite structure. They also discussed the idea that a highly conductive lowermost mantle could be the cause of changes in the length of day.

The electric conductivity of the lower mantle has been unknown until recently. Xu et al. (2000) measured the conductivity of perovskite under the topmost lower mantle

conditions and modeled the lower mantle conductivity profile by extrapolating the experimental data to much higher P and T . However, subsequently discovered high-spin to low-spin crossovers for iron (Badro et al., 2003) in (Mg,Fe)O ferropericlasite, perovskite, and post-perovskite (Murakami et al., 2004) are now known to affect the electric conductivity to a great extent. Iron spin crossover occurs in ferropericlasite in the middle to deep lower mantle (Lin et al., 2007a,b; Tsuchiya et al., 2006). While the spin state of ferrous iron in perovskite has been controversial (Badro et al., 2004; McCammon et al., 2008; Umemoto et al., 2010), it is generally accepted that ferric iron undergoes spin crossover in the mid-lower mantle (Stackhouse et al., 2007; Zhang and Oganov, 2006).

Lin et al. (2007b) and Ohta et al. (2007) first demonstrated the effect of iron spin crossover on the electric conductivity of (Mg,Fe)O ferropericlasite experimentally; the conductivity increased with increasing pressure but suddenly diminished above ~ 70 GPa at room temperature, similar to the pressure range of spin crossover in ferropericlasite. The electric conduction in high-spin ferropericlasite is dominated by a small-polaron process of electron hopping between ferrous and ferric iron sites (Dobson and Brodholt, 2000). The unpaired electrons in the 3d orbital play important roles in this process, but the number of unpaired electrons of ferric iron decreases from four to zero at the spin crossover, thus resulting in a marked reduction in the conductivity. Similar reduction in the electric conductivity of Fe-bearing MgSiO_3 perovskite has been also demonstrated at both 300 K (Ohta et al., 2010a,b) and high temperatures (Ohta et al., 2008b). These are likely caused by the spin crossover in ferric iron.

The electric conductivity of $(\text{Mg}_{0.9}\text{Fe}_{0.1})\text{SiO}_3$ post-perovskite has been measured to be on the order of 10^2 S m^{-1} , higher by three orders of magnitude than that of perovskite with iron in the low-spin state (Ohta et al., 2008b). This is attributed to the shorter Fe–Fe distance in post-perovskite structure, in which Mg and Fe form sheets inter-layering with SiO_6 (Figure 2). The conductivity of a peridotitic mantle material was also measured in a wide P – T range that covers almost all lower mantle conditions (Ohta et al., 2010a). The results showed $10^{1.5} \text{ S m}^{-1}$ at the base of the mantle. This is somewhat lower than that of single-phase $(\text{Mg}_{0.9}\text{Fe}_{0.1})\text{SiO}_3$ post-perovskite, because iron content in post-perovskite coexisting with ferropericlasite in a pyrolytic bulk composition is less than 5 mol% (Murakami et al., 2005; Sinmyo et al., 2011). Alternatively, subducted MORB crust (Ohta et al., 2010a) or metallic FeO possibly exsolved from liquid outer core with cooling (Frost et al., 2010; Ohta et al., 2012a,b) will have enhanced electric conductivity near the base of the mantle and may be responsible for strong electromagnetic coupling between the solid mantle and liquid core.

2.05.5 Geodynamic Consequences of Post-Perovskite

The role of phase transitions in mantle dynamics has historically been thought to be limited to the upper mantle, because until 10 years ago, only the olivine to spinel and the spinel to perovskite transitions were viewed as important. Before the discovery of post-perovskite, researchers focused on the issue of layered versus whole-mantle convection in the presence of

phase transitions (Christensen and Yuen, 1984, 1985; Honda et al., 1993; Schubert et al., 1975; Tackley et al., 1993) and the so-called avalanche events associated with the phase transition at 660 km depth. This phenomenon, first found by Christensen and Yuen (1985), in 2D models generated much greater attention in 3D (Honda et al., 1993; Tackley et al., 1993) and has attracted the attention of many geochemists (Allegre, 1997).

When the discovery of post-perovskite transition came along, it was recognized that this phase transition is fundamentally different from other mantle phase transitions because of its proximity to the CMB. The dynamical situation resembles the situation of the spinel to perovskite transition in the Martian mantle in which that phase transition may lie very close to the Martian CMB (Breuer et al., 1997; Harder and Christensen, 1996; Weinstein, 1995). Indeed, in the Earth's mantle, post-perovskite may act as a gatekeeper for mantle circulation descending to the CMB.

The D'' region has long been recognized as prone to dynamical instabilities because of the thermal boundary layer above the CMB (Jones, 1977; Stacey and Loper, 2007; Yuen and Peltier, 1980). The implications of the post-perovskite interpretation of the D'' layer, with the transition having a steep positive Clapeyron slope, are quite profound for the dynamics of the deep mantle. The rheology of post-perovskite may also be non-Newtonian and viscosity may be lower than that of perovskite because of the large stresses present at the boundary layer of mantle convection.

2.05.5.1 Dynamical Effects of Post-Perovskite in Earth

Geophysicists have examined the influence of post-perovskite on both thermal and thermochemical convection (Tackley et al., 2007; Yuen et al., 2007). Figure 15 shows the situation that arises for two Clapeyron slopes that depend on

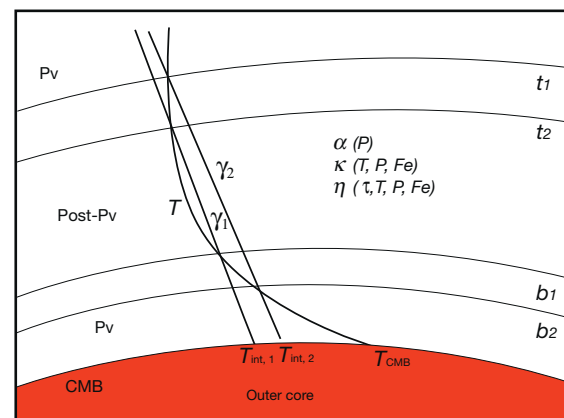


Figure 15 The intersections of the local one-dimensional geothermal with the Clapeyron slopes. T_{int} marks the temperature of the post-perovskite transition at the core–mantle boundary. The relative positioning between T_{int} and T_{CMB} determines whether double-crossing of the geotherm with the phase boundary occurs. Symbols t_1 , t_2 , b_1 , and b_2 indicate the top and bottom crossings. α , κ , and η represent, respectively, the thermal expansivity, thermal diffusivity, and viscosity of the lower mantle, and they depend on thermodynamic and chemical variables.

composition or how they would be crossed by a temperature curve associated with a thermal boundary layer above the CMB. We note that because of the uncertainties of the physical parameters, such as the depth variations of thermal expansivity and bulk moduli with depth, it is very difficult to ascertain the relative dynamical importance of each of these factors. With the post-perovskite transition dependent on composition, a great variety of complex behavior may arise, producing structures, such as the multiple crossings of the temperature curve by the two different types of post-perovskite transition (see Figure 15, where t_1 , t_2 , b_1 , and b_2 are the four intersections due to compositionally dependent phase boundaries).

The nature of double-crossing of the Clapeyron slope by the local geotherm was recognized early on by [Hernlund et al. \(2005\)](#) who emphasized at that time that the post-perovskite phase boundary can be employed to constrain many important thermal parameters in solid-earth geophysics, such as its phase change location relative to the melting curve of candidate mantle materials. This hypothesis has prompted seismological ventures into relating imaged structures in the D'' layer as thermal and compositionally influenced post-perovskite phase transitions, with attendant absolute temperatures and heat flow estimates ([Hutko et al., 2006](#); [Lay et al., 2006](#); [van der Hilst et al., 2007](#)).

From a dynamical standpoint, the 1.5% density change of the post-perovskite transition being may have impact on the local dynamics. This density change is equivalent to more than a thousand degree change in thermal buoyancy, because of the relatively low thermal expansion coefficient of around 10^{-6} in the deep lower mantle. Up to now, this dynamical effect has not been explored for post-perovskite transition at all and requires further examination. Latent heat effects can potentially be important as a feedback mechanism for exothermic phase transitions when coupled with variable viscosity and viscous heating ([Steinbach and Yuen, 1994](#)) and would require more investigation especially for the possibly low-viscosity post-perovskite regions in the deep mantle ([Ammann et al., 2010](#); [Cizkova et al., 2010](#)).

The dynamical influences of the phase boundary distortions are illustrated schematically in Figure 16 by a sketch of the phase boundary of post-perovskite (dashed curve) in the cold downwellings and hot upwellings. For temperature at the CMB greater than the temperature of the intercept in the post-perovskite transition, we note that beneath hot plumes, there can exist a patch of hot perovskite. Only as the Earth cools off does the perovskite hole disappear and become filled with post-perovskite. The buoyancy of the hot plumes is increased by the deflection of the lighter perovskite phase downward. In the downwelling, we see also the greater negative buoyancy provided by the phase boundary being pushed upward by the negative thermal contrast. For isotherm T_3 , there may be another zone of perovskite right above the CMB, delineating what is now called as the 'double-crossing' phenomenon ([Hernlund et al., 2005](#)). A Clapeyron slope dP/dT of $\sim 10 \text{ MPa K}^{-1}$ can cause undulations of $\sim 100 \text{ km}$ in the depth of the phase boundary for thermal perturbations of several hundred degrees.

Electric conductivity increases dramatically across the post-perovskite phase boundary ([Ohta et al., 2010b](#)) and aids the leakage of core electric currents to the mantle that can promote enhanced Joule heating at different sites over the CMB, following magnetic jerk events. But of greater dynamical interests are the thermal conductivity and viscosity of post-perovskite, which may, respectively, increase by around 50% and decrease by a factor of 50–100, as discussed in the preceding text. These properties would be conducive to the development of small-scale convection within the D'' layer ([Cizkova et al., 2010](#); [Samuel and Tosi, 2012](#); [Schott et al., 2002](#)).

From a dynamical standpoint, what new issues has the post-perovskite transition raised? First of all, we expect that the exothermic character of the post-perovskite transition should tend to promote instability in the D'' layer, increasing the heat flow and interior mantle temperature and increasing the number and time dependence of mantle plumes. Some of these predictions were confirmed by [Nakagawa and Tackley \(2004\)](#) for constant physical properties. Figure 17 shows a

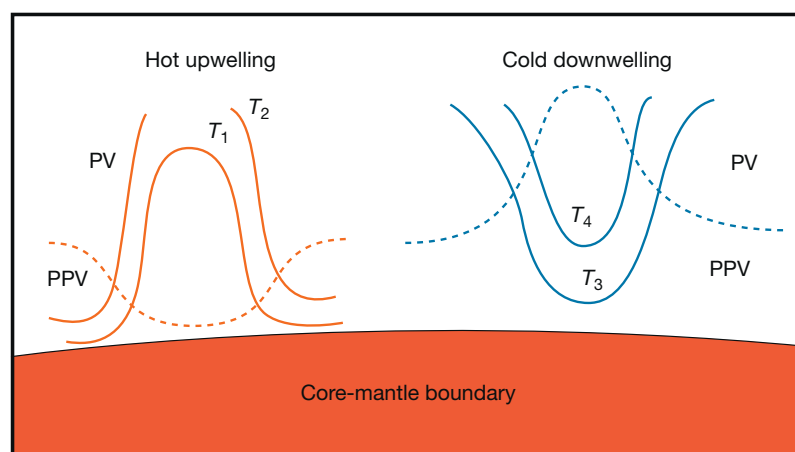


Figure 16 Schematic diagram showing the undulations of the phase boundary of the perovskite-to-post-perovskite transition due to hot upwellings and cold downwellings. T_1 , T_2 , T_3 , and T_4 are the isotherms associated with the two types of flow. Dashed curves show the undulations of the phase boundaries. There are an additional positive buoyancy for the upwelling and an additional negative buoyancy associated with the downwelling because of the positive Clapeyron slope of the post-perovskite transition ([Schubert et al., 1975](#)).

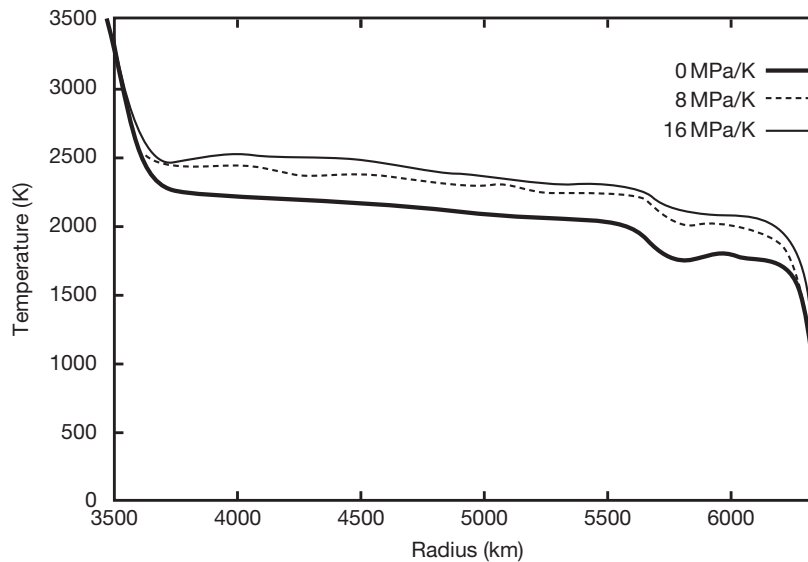


Figure 17 Time and horizontally averaged one-dimensional temperature profiles taken from two-dimensional Cartesian simulations of Nakagawa and Tackley (2004). A comparison is made for no post-perovskite transition to two different values of the Clapeyron slope from 8 to 16 MPa K⁻¹. The temperature increases in the interior from the presence of the post-perovskite transition.

comparison of the time-averaged vertical temperature profiles for three different cases: one without the post-perovskite transition, the second with a Clapeyron slope of 8 MPa K⁻¹, and the third with a slope of 16 MPa K⁻¹. There is an increase in the interior temperature with increasing Clapeyron slope, with a difference of 400 K between the reference case (no post-perovskite) and the case with the steepest Clapeyron slope. A more realistic model with variable viscosity would act to decrease the temperature difference because of negative buffering feedback from temperature-dependent viscosity (Tozer, 1972). The enhanced time dependence of boundary layer instabilities induced by the presence of the post-perovskite transition can be reduced by an increase of thermal conductivity with depth and a decrease of thermal expansivity with pressure (Matyska and Yuen, 2005; Tosi et al., 2010). In fact, increased radiative thermal conductivity can help to stabilize the chaotic situation in the D'' layer caused by exothermic post-perovskite transition (Matyska and Yuen, 2005).

The interaction of a cold descending slab with the D'' layer has always been an important dynamical problem. The piling up of slab material at the base of the mantle could play a role in the Earth's evolution. This topic becomes even more complex in the presence of post-perovskite. The possibility of slab material folding and piling at the base of the mantle and undergoing post-perovskite transition has been proposed by Hutko et al. (2006) based on strong lateral variations in seismic profiles. Lens-shaped post-perovskite structures, inferred from seismic imaging with ScS data (van der Hilst et al., 2007), have further attracted the attention of geodynamic modelers. Closely related issues of the seismologically observed complexity of the D'' layer include the relative effects of temperature and chemistry on the depth to and seismic visibility of the phase change and the distortion of the phase boundary by small-scale mantle convection.

Nakagawa and Tackley (2005, 2006) had carried out a series of models incorporating melting-induced chemical

differentiation, platelike behavior, multiple phase transitions, and compressibility to focus on the interaction of slabs and the D'' layer for models with horizontal wavelengths longer than about 65 km. van den Berg et al. (2010a,b) had performed a combined geodynamic and seismological investigation for scale lengths as small as 4 km, including the presence of subducted MORB. They evaluated the seismic imaging manifestation of the heterogeneous distribution of mineral phase and composition in the model by subjecting the finite-element modeling results to a decomposition into wave packets (Duchkhov et al., 2010). The spatial scales and orientations (i.e., dips) are restricted to those that can be resolved by ScS imaging of large global network datasets (van der Hilst et al., 2007; Wang et al., 2006). The short-scale resolution is derived from a matrix representation of the generalized Radon transform, by exploiting the concentration of wave packets, and this approach opens new pathways for joint seismic and geodynamic analysis of a local region.

We show in Figure 18 a zoom-in on the shear velocity variations of a post-perovskite lens structure of about 2000 km (top row), together with wave-packet decompositions at three different length scales. The wave speeds shown correspond to snapshots taken from thermal-chemical convection, the results having been converted from geodynamic output to seismic expressions by using mineral physics properties.

Three different scales $k=4-6$, corresponding to length scales of around 12 km, are considered in this figure. The three bottom rows show results of an analysis zoomed in at the top of the post-perovskite lenses, displaying clearly the visibility of the corrugated top of the post-perovskite layer and a thicker bottom post-perovskite layer. A Clapeyron slope of 6 MPa K⁻¹ is used in the simulation.

There is accumulating evidence that a strong viscosity contrast exists between perovskite and post-perovskite phases, with theoretical studies proposing a lower viscosity for post-perovskite (Ammann et al., 2010; Hunt et al., 2009). This is

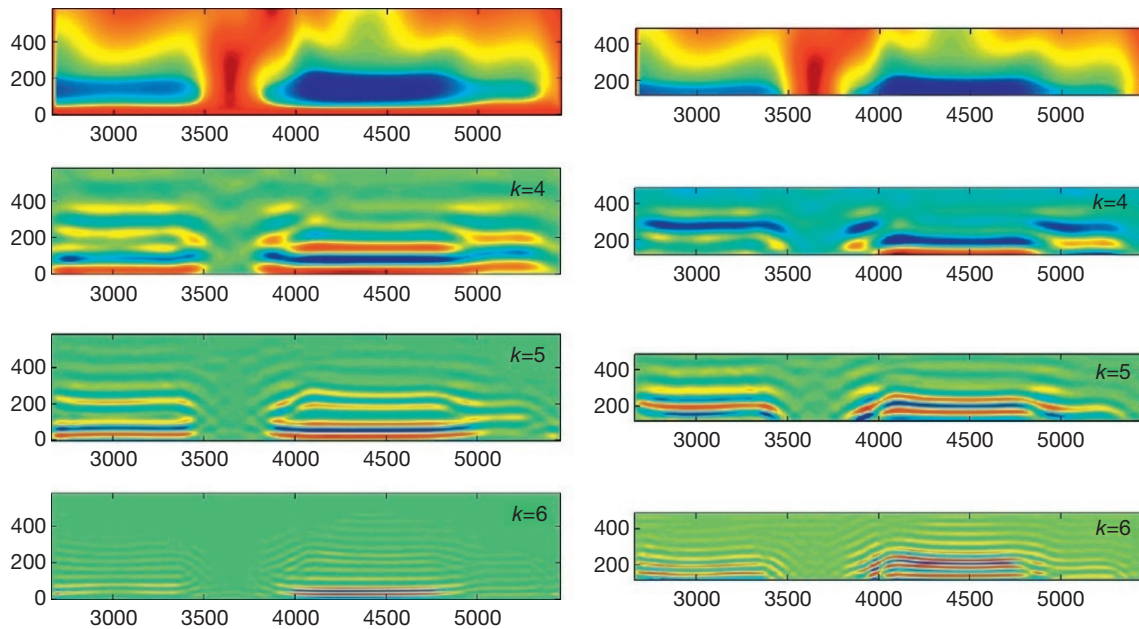


Figure 18 Wave-packet analysis for the observable character of shear-wave signatures obtained for a thermal–chemical convection with post-perovskite present. The model is two-dimensional and has a large aspect ratio (van den Berg et al., 2010a,b). We show here the seismic visibility of the lineaments of MORB crustal material in a background of pyrolitic material in the D'' region. The top row shows the variations in S-wave velocity. The second to bottom rows show the three wavenumber scales 4, 5, and 6 (van den Berg et al., 2010a), obtained from the wave-packet decomposition of the variations in shear-wave velocity. Left column, analysis of the bottom 600 km of the mantle; right column, results for a focused region showing the top of the post-perovskite lens.

supported by earlier inversions of intermediate-wavelength geoid anomalies and recent work based on the Earth's short-term rotational fluctuations (Cadek and Fleitout, 2006; Nakada and Karato, 2012; Tosi et al., 2009). Investigations focusing on this perovskite/post-perovskite rheological difference have found that the post-perovskite rheology can exert a noticeable influence on lower mantle dynamics and thermal evolution (Cizkova et al., 2010; Nakagawa and Tackley, 2011; Tosi et al., 2010), significantly amplifying the effects for post-perovskite assumed to have the same viscosity as perovskite.

Samuel and Tosi (2012) found that the presence of weak post-perovskite enhances heat transfer across the bottom thermal boundary layer, thus producing higher temperatures, reducing viscosities, and giving rise to considerably larger convective velocities. Small-scale fast convection is induced within the D'' layer and enhances local mixing. Figure 19 shows the surface Nusselt number, which corresponds to the averaged surface heat flow and root-mean-squared velocity as a function of time for four different viscosity contrasts, ranging from ten times greater viscosity for post-perovskite to 0.01 lower viscosity for post-perovskite. There is a sharp reduction of the time scales when post-perovskite viscosity is decreased and a correspondingly rapid increase in the mean velocity. Mixing time was found to decrease dramatically with a 0.01 post-perovskite to perovskite viscosity ratio (Samuel and Tosi, 2012). With the development of post-perovskite in the secularly cooling deep mantle, the surface heat flow would increase dramatically that might cause a mantle overturn at 2.6 Byr ago (Breuer et al., 1996), manifested in a series of geologic and geobiological signatures (Maruyama et al., 2007). The time for the appearance of post-perovskite in the deep mantle is still uncertain but

remains an important question in mantle evolution, especially in view of recent paper on the melting curve of pyrolite (Nomura et al., 2014), which found a lower melting temperature than previous results for pure MgSiO_3 minerals.

Mantle convection can be viewed dynamically as a non-linear system (Bohr et al., 1998) because many thermodynamic parameters and transport properties such as thermal conductivity and viscosity depend sensitively on both temperature T and pressure P . The evolution of the Earth's mantle and core depends sensitively on the interactions among the various input parameters, such as the material properties and the time-varying boundary conditions. Figure 20 shows a comparison of the dynamical time scales for the three different models, ranging from constant thermodynamic and thermal transport properties to variable thermodynamic parameters and thermal conductivity. The last case has a post-perovskite transition but with post-perovskite having the same viscosity as perovskite. Much faster time scales are present with constant properties, and the influences of variable thermal expansivity and the greater post-perovskite thermal conductivity are to greatly slow down the dynamics. In order to estimate the viscosity of the lower mantle from slab remnants inferred from seismic tomography (e.g., Li and Yuen, 2014; van der Meer et al., 2010), it is important to consider all physical parameters, such as thermal expansivity, conductivity, and chemical heterogeneities.

Figure 21 from Tosi et al. (2013) displays a comparison of the temperature fields for five different models. We show representative snapshots of selected simulations that were run until they reached a statistical steady state and the panels feature constant thermal expansivity α and conductivity k (Figure 21(a)), variable α and constant k (Figure 21(b)),

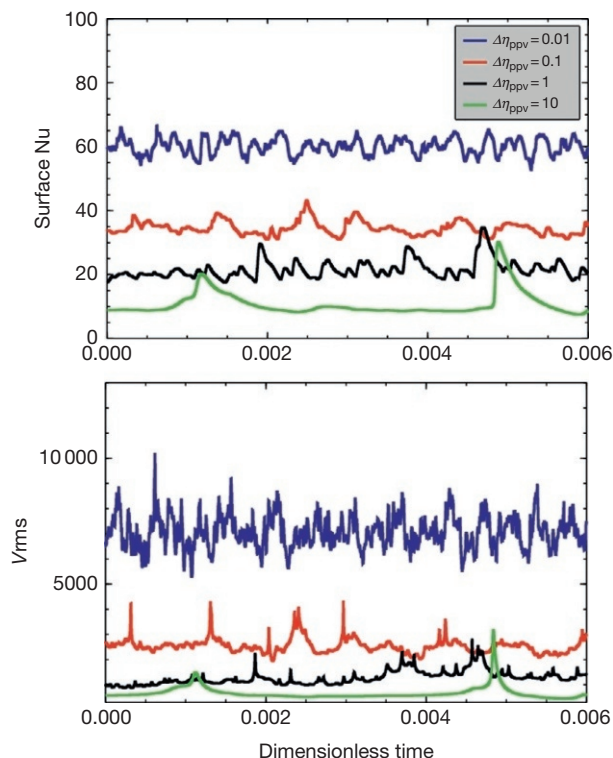


Figure 19 Influence of post-perovskite viscosity (η_{ppv}) on dynamical time scales. The averaged value of the surface heat flow and the root-mean-squared velocity of 2D mantle convection with post-perovskite are shown for various ratios of viscosity contrast between perovskite and post-perovskite, ranging from a stiffer post-perovskite to a much softer post-perovskite. In spite of the small volume occupied by post-perovskite in the mantle, the rheology of post-perovskite has strong influence on the time scales of the evolution of global mantle dynamics.

constant α and variable k (Figure 21(c) and 21(d)), and variable α and k (Figure 21(d) and 21(g)). Figure 21 shows temperature perturbations from the laterally averaged temperature profile. From Figure 21, it is quite evident that the influence of variable expansivity and conductivity on mantle convection is dramatic. When both parameters are held constant, the temperature field shows the character prevalent for convection at relatively high Rayleigh numbers with internal heating. The flow is dominated by cold downwellings, which, despite the viscosity jump between upper and lower mantle, sink straight to the CMB and accumulate there, cooling the deepest part of the mantle and producing the locally elevated post-perovskite lenses. Because of the limited temperature jump across the bottom thermal boundary layer, hot upwellings are generally weak and short-lived. In the presence of variable thermal conductivity, the mantle temperature increases sufficiently for plumes to be suppressed and post-perovskite forms only at places where cool downwellings reach the deep mantle. The distribution of thermal conductivity is dominated by pressure effects except in the core of cold slabs where it attains its highest values when temperature dependence is included. We emphasize here that despite their high conductivity, slabs do not heat up efficiently via conduction since they sink very rapidly because of the generally low viscosity of the surrounding hot mantle. The rapid sinking

increases surface plate velocities. Using constant properties or just variable expansivity, plate velocities are in the range of a few cm a^{-1} or a fraction of cm a^{-1} , respectively. With variable conductivity, they can become up to one order of magnitude larger (e.g., the peak surface velocity associated with the slab of Figure 21(f) is around 30 cm a^{-1}). The differences between models featuring P -dependent and P - and T -dependent k are minor, both qualitatively (compare Figure 21(c) and 21(d)) and quantitatively. In terms of temperature distribution, the largest differences are attained in the lower mantle and amount to 0.02 (74 K).

When both variable α and k are considered together (Figure 21(d) and 21(g)), we find another convective regime. Because of the temperature increase caused by the elevated thermal conductivity at depth and the modified buoyancy properties induced by variations of thermal expansivity, both up- and downwellings assume equal importance. In particular, whether we use either A or B models, convection shows an increased propensity toward local layering, with slabs that are often trapped in the transition zone before sinking into the lower mantle where the associated cold thermal anomaly also tends to broaden. Occasionally, slab detachment caused by a period of prolonged stagnation can also be observed, as shown in Figure 21(g). Furthermore, the slowing effect exerted by variable expansivity helps to reduce high surface velocities to more realistic plate values from ~ 4 to 5 cm a^{-1} .

Self-consistent mineral physics within a thermodynamic framework (Connolly, 2005) has been employed by Nakagawa et al. (2010, 2012) to study the influence of oceanic crust on thermal–chemical mantle convection with post-perovskite transition. Models were originally run for 3D geometry (Nakagawa et al., 2010), but to obtain proper resolution, a more modest spherical annulus geometry (Nakagawa et al., 2012) was employed in order to resolve the CMB region at 10 km radial resolution and has 30 tracers per cell to track accurately the composition and melt fraction. In Figure 22, we show their results for temperature, composition, and seismic perturbations in bulk sound velocity and shear waves at a time of 4.5 Gyr from the beginning and for bulk composition of MORB and harzburgite and pyrolite taken from Ringwood (1985). We can see that the cold subducted slabs are deformed greatly in the deep mantle and have a tendency to produce folded structures above the CMB (Hutko et al., 2006). The basaltic crust is separated from subducted slabs above the CMB and then piles up to form large-scale compositionally distinct structures. Upwelling plumes are observed to rise from the edge of the basaltic piles or between the pooled cold regions. In the shear velocity field, post-perovskite increases the velocity contrast between the piles and the cold pool between the piles. On the other hand, post-perovskite reverses the sign of the bulk sound velocity contrast, making the cold region slower than the piles. This causes the correlation between the shear and bulk sound velocities to be small or negative in the bottom part of the mantle and positive above this region. These results indicate that both mineral physics together with geodynamics must be employed together to unravel the complicated structures in the D'' layer, which come from the dynamics of the slab interacting with the D'' layer and the delicate balance among thermal, phase, and compositional influences on seismic structure.

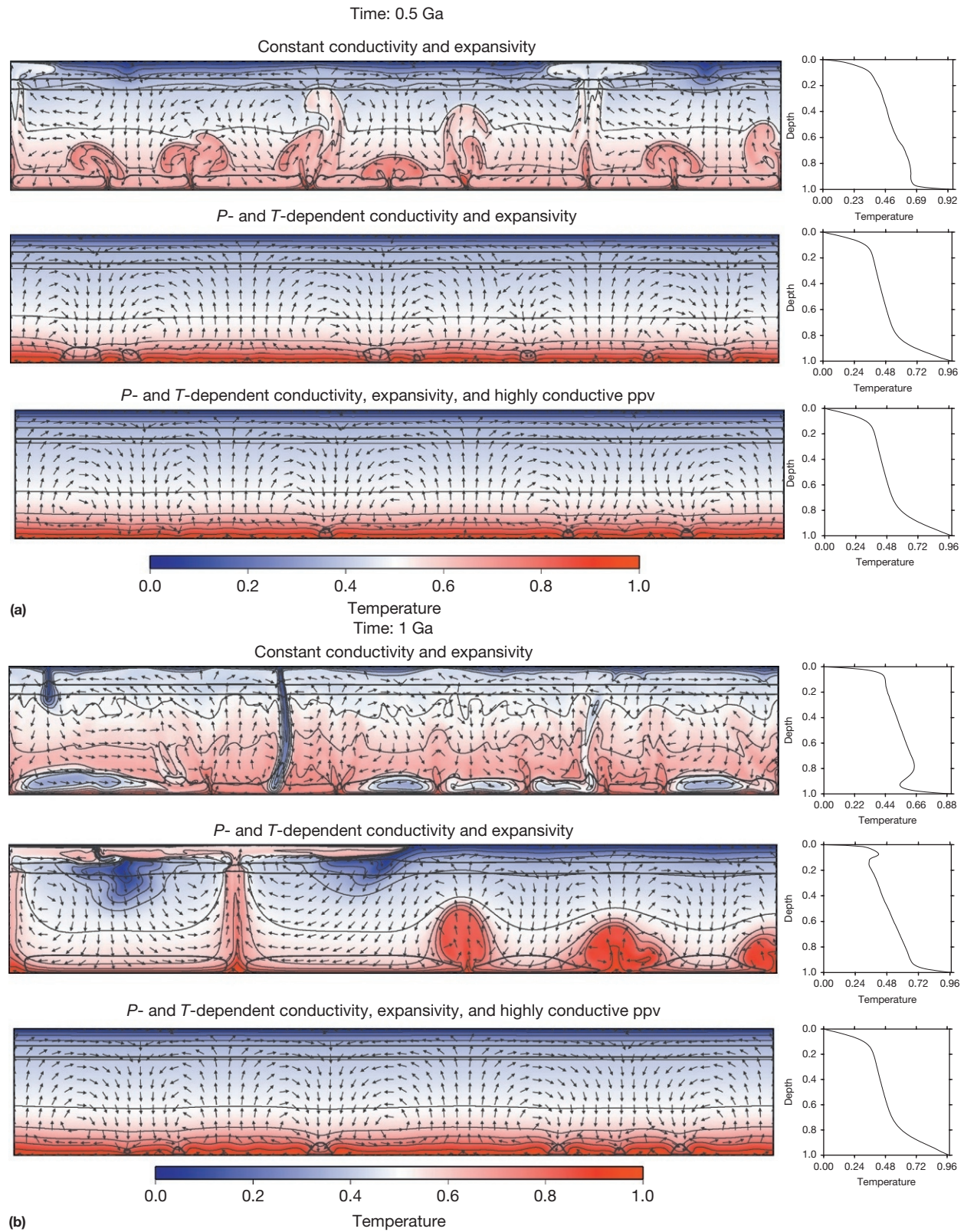


Figure 20 (Continued)

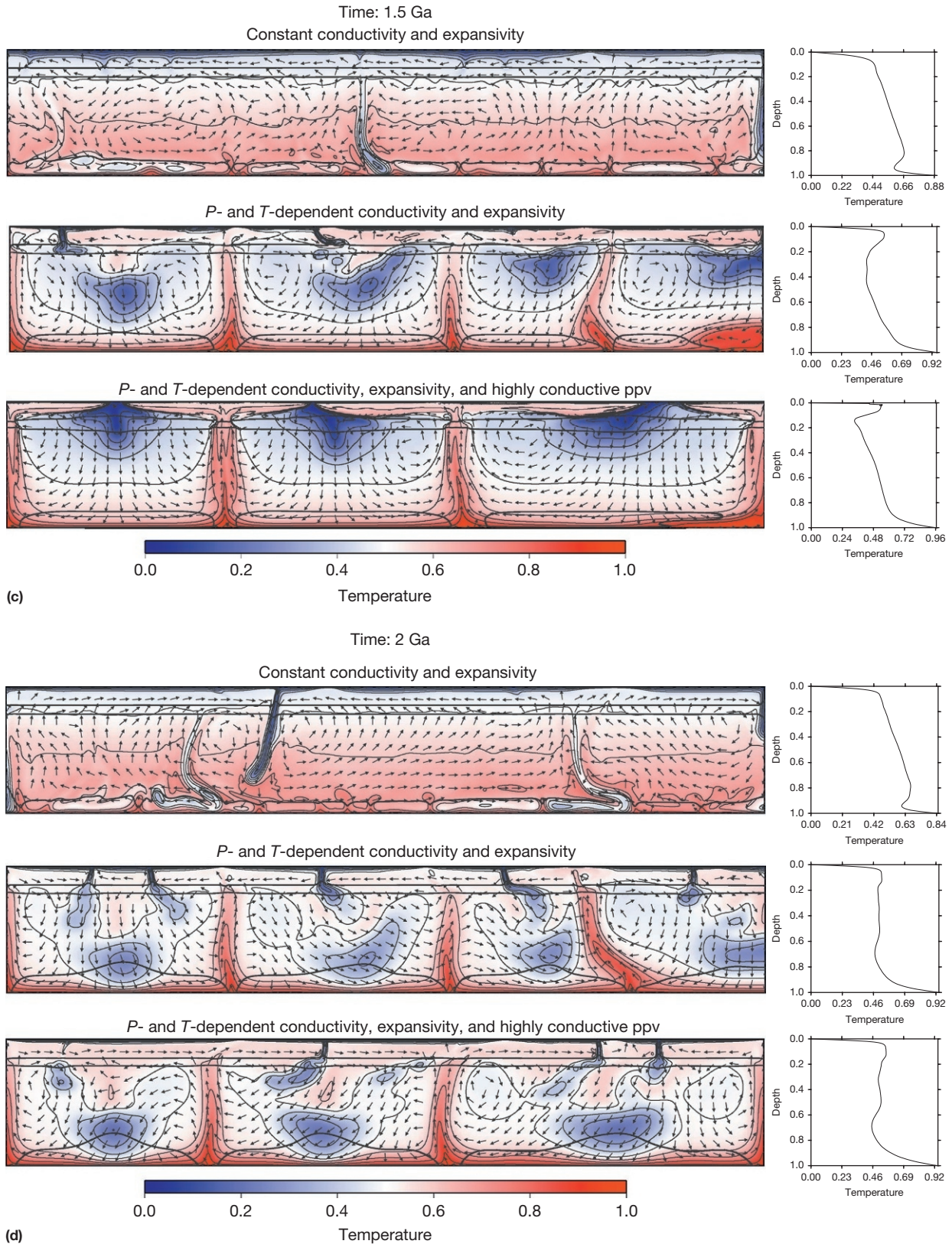


Figure 20 Comparison of the dynamical scales among models with constant thermal conductivity and conductivity, temperature- and pressure-dependent thermal conductivity and expansivity, and temperature- and pressure-dependent thermal conductivity and expansivity in addition to a highly conductive post-perovskite (e.g., [Ohta et al., 2012a,b](#)). Both the spinel to perovskite and perovskite to post-perovskite transitions are included in all models. The rheology is temperature- and pressure-dependent ([Tosi et al., 2013](#)). We note that the time scales are fastest for the constant thermal conductive and expansivity model and slowest when the more conductive post-perovskite is employed.

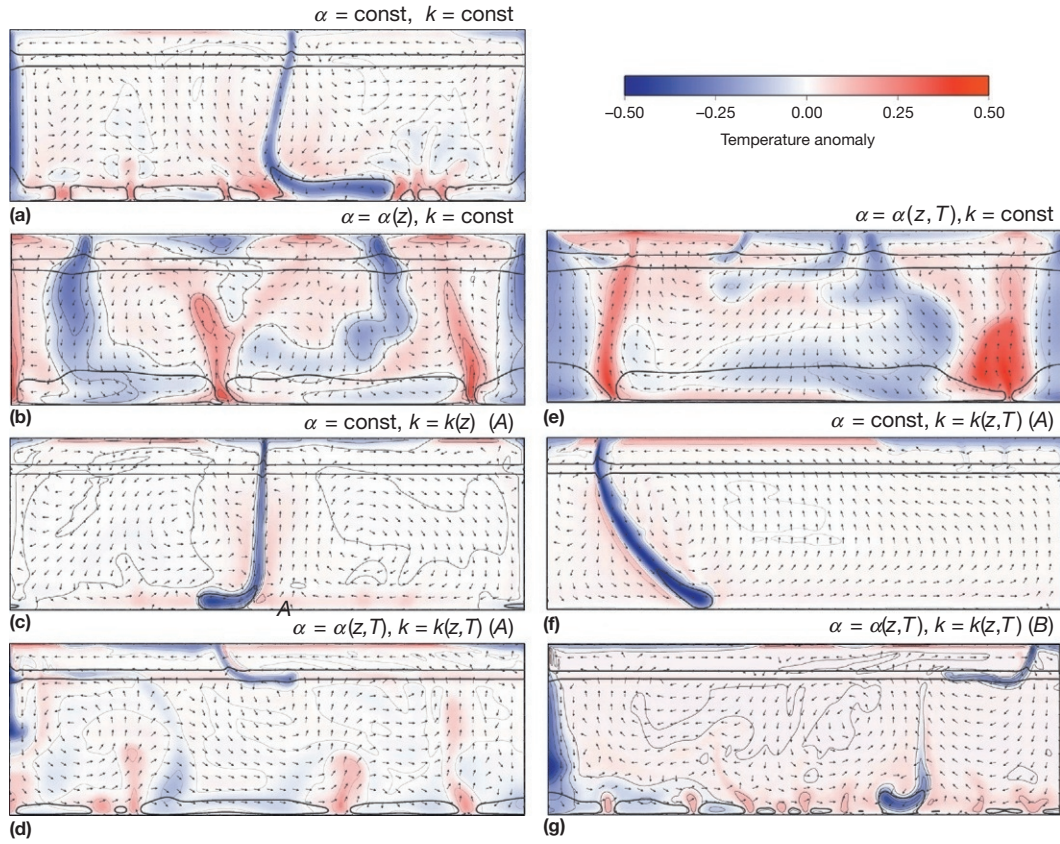


Figure 21 A comparison of the temperature anomaly fields and velocity vectors for seven different models. Models feature constant thermal expansivity and thermal conductivity (panel a), variable thermal expansivity and constant thermal conductivity (panels b and e), constant thermal expansivity and variable thermal conductivity (panels c and f), and both variable thermal conductivity and expansivity (panels d and g). Arrow indicates the direction of the flow field. Two different depth-dependent thermal conductivity models (A and B) have been considered. Reproduced from Tosi N, Yuen D, de Koker N, and Wentzcovitch RM (2013) Mantle dynamics with pressure- and temperature-dependent thermal expansivity and conductivity. *Physics of the Earth and Planetary Interiors* 217: 48–58, <http://dx.doi.org/10.1016/j.pepi.2013.02.004>.

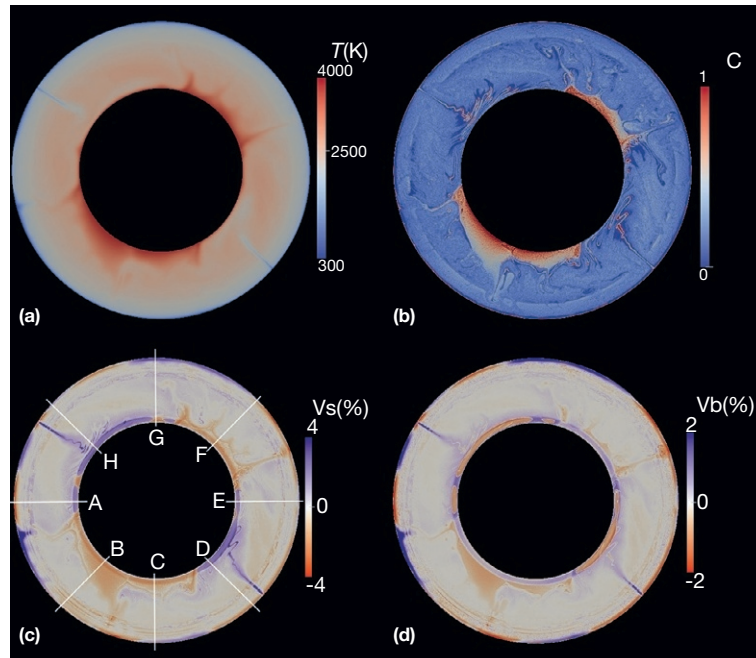


Figure 22 Temperature, composition, shear velocity, and bulk sound velocity from high-resolution two-dimensional convection in a spherical annulus. Snapshots are taken at 4.5 Ga from the beginning of the simulation (Nakagawa et al., 2012). The thermodynamic approach to mineral physics from Connolly (2005) has been employed to calculate the seismic expressions from convection simulation.

2.05.5.2 Heat Flux Constraints

Assuming that the D'' seismic discontinuity is a manifestation of the post-perovskite phase transition, temperature in the lowermost mantle can be estimated from the phase diagram for an assumed composition and mineral assemblage. Moreover, a shear-wave velocity reduction observed below the D'' discontinuity may be caused by back-transformation from post-perovskite to perovskite due to rapid increase in temperature in the thermal boundary layer above the CMB. This 'double-crossing' scenario (the lowermost mantle geotherm intersects the phase boundary twice) was originally proposed by [Hernlund et al. \(2005\)](#) and can be used to constrain the temperature gradient in D'' and, for a given choice of thermal conductivity, the associated heat flow (e.g., [Hernlund et al., 2005](#); [Lay et al., 2006](#); [van der Hilst et al., 2007](#)).

[Nomura et al. \(2014\)](#) had found that the solidus temperature of pyrolite can be some five hundred degrees lower than the melting temperature for perovskite mineral ([Boehler, 1996](#)). This result has important implications for the amount of post-perovskite in the lower mantle and the amount of coverage of post-perovskite over the global CMB surface. [Figure 23](#) displays the coverage of post-perovskite (gray color) over the CMB surface. This snapshot was taken from numerical simulations in 3D spherical convection using very high-resolution and statistical techniques for quantifying the relationships of depths of double-crossings of the post-perovskite transition developed in 3D convection ([Monnereau and Yuen, 2010](#)). The global coverage over the CMB surface by post-perovskite today is an important factor in the overall heat flux as a function of mantle evolution and should be a probed

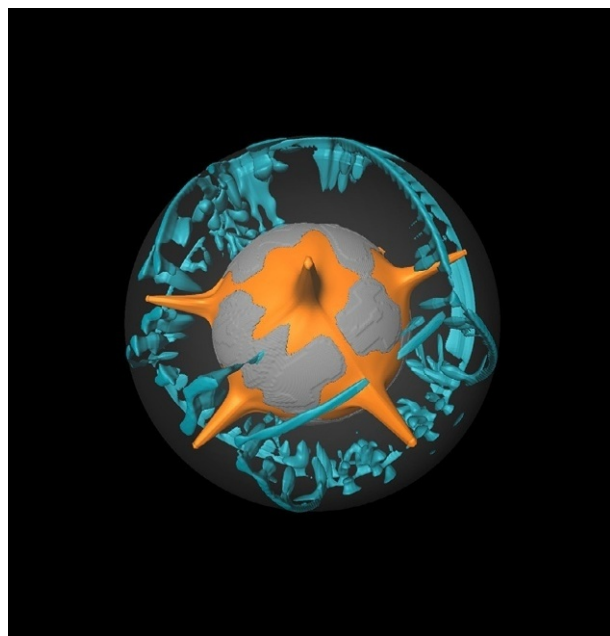


Figure 23 Snapshot of 3D spherical convection showing the coverage of post-perovskite (gray color) over the core–mantle boundary surface. Blue and orange colors denote cold and hot material, respectively. Calculations are taken from [Monnereau and Yuen \(2007, 2010\)](#), in which both thermal conductivity and thermal expansivity are depth-dependent. The viscosity is depth-dependent with a jump at 670 km depth. Three mantle phase transitions are included.

with detailed seismic arrays because from the estimate of this quantity, we can derive better constraint on the timing of post-perovskite appearance in the lower mantle.

2.05.5.3 Dynamical Effects of Post-Perovskite in Other Planets

The interiors of exosolar planets ([Marcy and Butler, 1995](#)) represent a new fertile field for planetary scientists and astronomers to research together. Most such planets found up to now are much larger than the Earth, typically the size of Jupiter. But recently, several planets, dubbed super-Earths, have been detected near the star Gliese 876, with estimates of about seven Earth masses. A nearby star Gliese 581 hosts several more of these large planets, with some being rocky. The mantles of these rocky planetary interiors represent a frontier area for mineral physics and dynamical modelers, as post-perovskite will play an important role. The mineralogy of super-Earth interiors will undergo additional structural changes at extreme (TPa) pressures ([Coppari et al., 2013](#); [Umemoto et al., 2006b](#)). Geodynamacists have begun to model the mantle dynamics of exosolar planets ([O'Neill and Lenardic, 2007](#); [Tackley et al., 2013](#); [Valencia et al., 2007a,b,c](#)) but very few have included the influences of phase transitions, in particular the perovskite-to-post-perovskite transition and the higher pressure decomposition of post-perovskite ([Umemoto et al., 2006b](#)).

[van den Berg et al. \(2010b\)](#) modeled the time-dependent dynamics of exosolar planets within the framework of a two-dimensional Cartesian model and the extended Boussinesq approximation and included the post-perovskite transition and its deeper decomposition to the oxides ([Umemoto et al., 2006a](#)). The mass of the super-Earth models considered is eight times the Earth's mass and the thickness of the mantle is 4,700 km. The effects of depth-dependent properties have been considered for the thermal expansion coefficient, the viscosity, and thermal conductivity. The viscosity and thermal conductivity are also temperature-dependent. The thermal conductivity has contributions from phonons, photons, and electrons. The last dependence comes from the bandgap nature of the material under high pressure and increases exponentially with temperature and kicks in at temperatures above 5,000 K. The thermal expansivity decreases by a factor of 20 across the mantle because of the high pressure, greater than 1 TPa. They considered three phase transitions: the spinel to perovskite, the post-perovskite, and the post-post-perovskite decomposition in the deep lower mantle, for which the Clapeyron slope is strongly negative -18 MPa K^{-1} ([Umemoto et al., 2006a](#)), inducing layered convection in the deep portion of the exoplanet.

Their results show that because of the multiple phase transitions and strongly depth-dependent properties, particularly the thermal expansion coefficient, most of the planetary interior is strongly superadiabatic initially in spite of a high surface Rayleigh number, because of the presence of partially layered and penetrative convective flows throughout the mantle, unlike convection in the Earth's mantle. This period of superadiabaticity can last a very long time, more than a couple of Ga. An outstanding influence of electronic thermal conductivity is to heat up the bottom boundary layer quasi-periodically, giving rise to strong coherent superplumes, which can punch their way to the upper mantle and break up the layered convective

pattern and may give rise to planetary-scale super volcanism. Figure 24 displays representative snapshots of the temperature field and corresponding stream functions for three model cases all with the negative Clapeyron slope, with the same temperature contrast $\Delta T = 10\,000$ K.

The only difference in the models is the thermal conductivity, with models A and B having constant conductivity, while model C has contributions from phonons, photons, and electrons. The last component has an exponential dependence in T . The different degree in the style of layered convection near the bottom post-post-perovskite decomposition boundary can be clearly discerned in these frames, in particular in the distribution and spacing of the contour lines in the stream function. Model A with a decrease factor of thermal expansivity across the mantle of 0.1 shows limited interaction between the endothermic phase boundaries, with hot plumes crossing the phase boundary in several locations. The middle row of snapshots for model B with thermal expansivity contrast of 0.05 illustrates that a penetrative convective flow regime in the stream function with flow fields concentrated in the top half of the mantle and the bottom circulation is driven by the convection cells in the shallow mantle. As in the A model, the flow is driven by the cold downwellings. The temperature snapshots reveal an increased layering at the post-post-perovskite boundary at the bottom, as indicated by the mushroom-shaped plumes, which show only limited penetration of the deepest phase boundary. The increase in layering between models A and B is related to the smaller value of the thermal expansivity near the bottom post-perovskite decomposition resulting in a higher effective phase buoyancy parameter that scales inversely with respect to thermal

expansion coefficient (Christensen and Yuen, 1985). A similar type of layered penetrative convection was observed in Breuer et al. (1997) in a model for the Martian mantle.

In contrast to the constant thermal conductivity models, model C has a variable thermal conductivity $k(T,P)$ model with a strong contribution from electron thermal conductivity k_e near the bottom of the mantle, where temperatures are in excess of 5,000 K. The high conductivity at the base of the mantle results in an increased heat flow into the bottom post-perovskite decomposition layer, producing episodic occurrence of massive mantle plumes that break through the phase boundary, as illustrated by the hot plume near the middle of the temperature frame and corresponding high vertical velocity shown by the very narrow spacing in the stream functions. These events may trigger volcanism on the surface of exoplanets, which may be detectable someday by space telescope (Kaltenegger et al., 2011). We depict this scenario in Figure 25.

The viscosity of the post-perovskite lower mantle in exosolar planet has attracted the attention of mantle rheologists, and there is currently a debate between computational mineral physicists (Ammann et al., 2010), who argued from dislocation theory and experimental rheologists (Karato, 2011, 2013), who relied on ideas from diffusion of vacancies. Ito and Toriumi (2007) had shown from large-scale MD simulations of MgO that a viscosity maximum can be found under high enough pressure. Using high-resolution boundary-element method simulations, Morra et al. (2010) had found that pulsating plumes can also be developed by a Rayleigh–Taylor type of instability from these types of viscosity ‘hills’ in the Earth’s

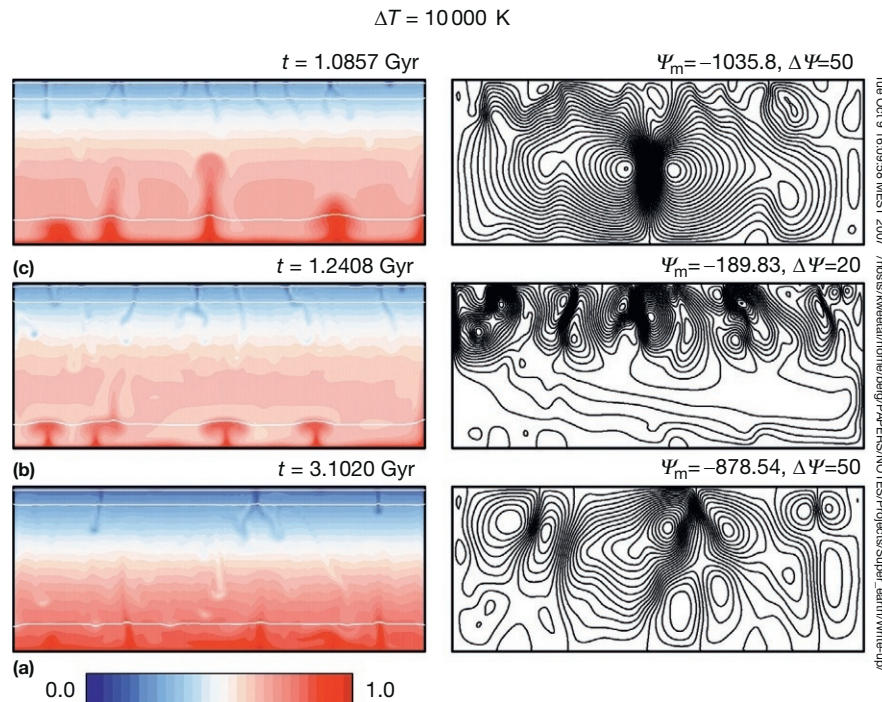


Figure 24 Temperature and stream functions associated high-resolution two-dimensional simulations of convection in an exoplanet. Three different models have been considered in these time-dependent runs (van den Berg et al., 2010a,b). A temperature contrast of $10\,000^\circ$ across the exoplanet with a mass eight times that of the Earth has been assumed. Decomposition of post-perovskite at ultrahigh pressures close to 1 Tpa (Umemoto et al., 2006a) has been employed with a strong negative Clapeyron slope of -18 MPa K^{-1} . The thermal conductivity model has contributions from phonons, photons, and electrons. Rheology is only temperature-dependent with a lateral contrast of 10000.

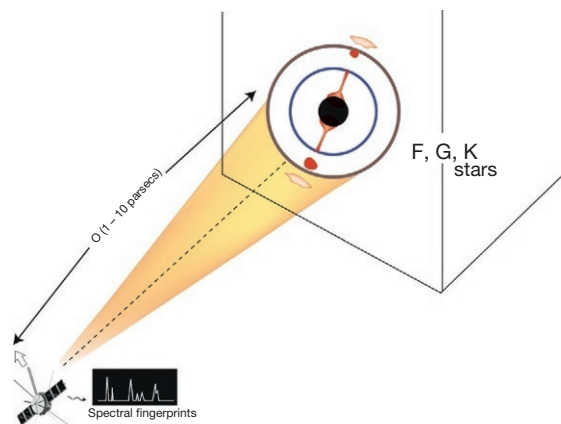


Figure 25 Possible future scenario of space telescopic detection of volcanic gas (Kaltenegger et al., 2011) coming from pulsating plumes in exosolar planets due to the interaction (Morra et al., 2010) between an upwelling and a viscosity hill predicted by the work of Ito and Toriumi (2007) and Karato (2011, 2013).

mantle. Karato (2011, 2013) had developed a new idea of viscosity maximum in the post-perovskite mantle, which is followed below by a low-viscosity deep mantle in large exosolar planets. The style of exoplanetary convection between the two rheological models (Ammann et al., 2010; Karato, 2011) may be tested by searching for spectral fingerprints from emitted volcanic gases (see Figure 24), where we would expect to more volcanic gases to be emitted by the plume pulsation model.

2.05.5 Conclusions

The extensive investigations of the post-perovskite phase described here represent a major advance in our understanding of deep mantle mineralogy, transport properties, and dynamics. Given the predominance of silicate perovskite in the lower mantle, the importance of discovery and characterization of post-perovskite brought multidisciplinary focus on this new phase. Many questions remain about post-perovskite in the Earth and in other planets, and the breadth of investigations will continue for much time to come, ultimately modifying some of the findings reported in this summary.

Acknowledgments

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2.06 Earth's Core: Iron and Iron Alloys

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2.06.1 Introduction

Earth's core plays a fundamental role in the evolution of our planet. The dominant composition of Earth's core is that of iron alloyed with 5–15% nickel. As Earth cools, the inner core grows, crystallizing from the liquid outer core, containing ~5–10% light elements, to form a solid inner core, with ~2–3% light elements (Alfè et al., 2002a; Jephcoat and Olson, 1987; Poirier, 1994; Stixrude et al., 1997). The release of latent heat of fusion, together with chemical buoyancy arising from the enrichment of the outer core with light elements, provides driving forces for the fluid flow responsible for the geodynamo and, hence, for Earth's magnetic field. The heat released from the core helps drive mantle convection, which, in turn, leads to surface features such as volcanism and plate tectonics. Because the inner core is sitting within the liquid outer core, it is isolated from the rest of Earth; however,

coupling with the outer core and mantle (e.g., geomagnetic and gravitational) prevents its motion from being entirely independent, allowing it to only super-rotate and wobble.

The only direct observations of Earth's core come from seismology; therefore, any credible mineralogical model has to match exactly the seismic observations. Increasingly accurate seismic observations have shown Earth's inner core, in particular, to be far more complex than had previously been thought. The current seismological models reveal an inner core that is anisotropic, layered, and laterally heterogeneous, but the origins of these characteristics are not yet fully understood. It is generally considered that the anisotropy reflects the preferred orientation of the crystals present, which could either have arisen during inner-core crystallization or developed over time through solid-state flow; these two mechanisms have vastly different implications for core evolution. The observed layering may have been caused by changes in chemical

composition, crystal structure, preferred orientation, or some combination of all three. Again, these imply very different core processes and evolution. The lateral heterogeneity could be because of uneven crystallization processes or even translational motion of the inner core itself. The origin of the anisotropy, layering, and lateral inhomogeneity is fundamental to understanding and constraining evolutionary models for Earth's inner core, and the mineralogical model must reflect this complex structure.

Mineral physics also has an important role to play in our understanding of the processes going on in the outer core. Knowledge of the thermoelastic properties of candidate liquid iron-alloys can be compared with seismological observations and thus lead to models for the composition of the outer core. Estimates for the dynamic properties of liquids such as diffusivity and viscosity can be incorporated into the magnetohydrodynamic equations that quantify the magnetic field. Furthermore, mineral physics can provide values for thermodynamic quantities that can be put into thermal evolution models of core formation, leading to timescales for inner core growth and quantification of the heat budget of Earth.

In order to place fundamental constraints on the properties of Earth's core, it is essential to know the behavior of iron and iron alloys at core conditions. In particular, the key questions to resolve are the following: (1) What is the most stable phase(s) of iron present in the inner core? (2) What are the elastic properties of the stable phase(s) (at core pressures and temperatures)? (3) What are the rheological properties of these candidate solid phases? (4) Do the combined thermoelastic and rheological properties of iron alloys lead to a comprehensive model for inner core composition, evolution, anisotropy, and layering? In addition, (5) what is the temperature of Earth's core? (6) What are the thermodynamic properties of candidate liquid iron-alloy phases? (7) What is the thermal conductivity of the outer core? (8) What are the rheological properties of these phases? (9) What is the composition of the outer core? Notwithstanding the difficulties in answering any single one of these questions, the combined answers to them all should exactly match the models inferred from seismology.

2.06.2 Seismological Observations of Earth's Core

2.06.2.1 Preliminary Reference Earth Model and Beyond

One-dimensional (1D) global seismological models for Earth's core, such as the Preliminary Reference Earth Model (PREM) (Dziewonski and Anderson, 1981), give bulk elastic properties as a function of depth via compressional and shear-wave velocity profiles and free oscillation data. Although these models tell us nothing about the exact composition or temperature, they do give fairly robust measurements for pressure and density as well as elastic moduli, such as incompressibility and shear modulus, by which compositional models can be tested. Since PREM, there have been a number of refinements of the seismological model (such as IASP91 (Kennett and Engdahl, 1991) and AK135 (Kennett et al., 1995)), which show subtle differences in the detailed velocity profiles, but they are generally consistent with each other. More complex structures of Earth have been observed with 3D imaging generated using seismic tomography; this shows how the wave velocities vary laterally as well as

radially, generating a 3D representation of wave velocities throughout Earth (see, e.g., Romanowicz, 2003 for a review).

2.06.2.2 Anisotropy, Layering, and Hemispherical Variations in the Inner Core

It has been well established that the inner core exhibits a significant anisotropy, with P-wave velocities $\sim 3\%$ faster along the polar axis than in the equatorial plane (Beghein and Trampert, 2003; Creager, 1992; Oreshin and Vinnik, 2004; Song, 1997; Song and Helmberger, 1993; Song and Xu, 2002; Sun and Song, 2002). Early models for the inner core suggested that this seismic anisotropy had cylindrical symmetry, with the symmetry axis parallel to Earth's rotational axis. More recent seismic observations suggest that, as well as being cylindrically anisotropic, the inner core may, in fact, be layered, with hemispherical variations in anisotropy (Figure 1). The evidence is for a seismically isotropic or weakly anisotropic upper layer, with lateral variations in thickness ranging between ~ 100 and 400 km, overlying an irregular, nonspherical transition region to an anisotropic lower layer (Ishii and Dziewonski, 2003; Ouzounis and Creager, 2001; Song and Helmberger, 1998; Song and Xu, 2002; Sun and Song, 2008). The existence of an isotropic upper layer implies that the magnitude of the seismic anisotropy in the lower inner core should be significantly greater than previously thought, possibly as much as $5\text{--}10\%$ (Ouzounis and Creager, 2001; Song and Xu, 2002). The observed layering also implies that the upper and lower inner core could be compositionally or structurally different.

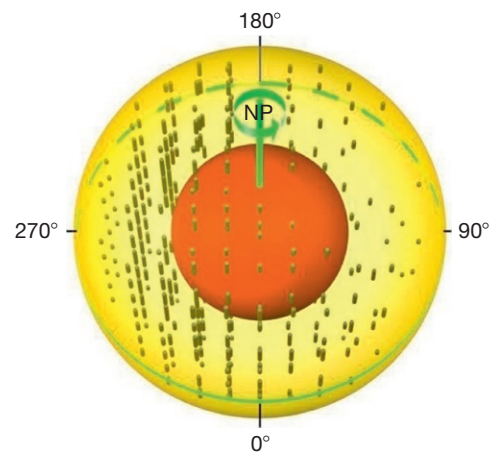


Figure 1 Schematic of isotropic upper-inner-core and anisotropic lower-inner-core structure from the data of Sun and Song (2008). Line length represents the magnitude of the P-wave anisotropy. The transparent outer surface is the inner core boundary (at radius 1220 km). The opaque inner sphere is the lower inner core (slightly less than half of the inner core radius). The sticks represent the alignments of iron crystals in the outer part of the inner core. The longer the stick is, the higher the degree of alignment and the stronger the seismic anisotropy. The fast direction is parallel to the spin axis. NP stands for the North Pole. The anisotropy in the top 100 km is weak. The anisotropy at greater depths is stronger in the western part than in the eastern part. The form of anisotropy in the inner core is different from that in the outer part. Credit: Illustrations by Precision Graphics; image from Phys.org <http://phys.org/news124372414.html>.

With this recently observed complex structure of the inner core, the question arises as to the mechanisms by which such anisotropy and layering can occur, and the nature of the seismic boundary. The isotropic layer could be the result of either randomly oriented crystals (containing, e.g., body-centered cubic (bcc), face-centered cubic (fcc), and/or hexagonal close-packed (hcp) iron) or a material with a low intrinsic anisotropy. The anisotropic lower layer is thought to be caused by the preferred orientation of aligned crystals (Anderson, 1989), possibly, although not necessarily, of an iron phase different from the upper layer. The inner core could therefore, for example, be composed entirely of bcc iron, entirely of hcp-Fe, or some combination of the two.

There are three hypotheses of how the anisotropy and layering could have occurred:

1. Yoshida et al. (1996) have suggested a driving mechanism whereby the inner core grows more rapidly at the equator than at the poles, giving rise to a flattened sphere. In order to maintain hydrostatic equilibrium, this ellipsoidal inner core would have to continuously deform as it grows, resulting in stress-induced recrystallization. Figure 2 shows the flow lines resulting from their calculations. In this model, the older material will have undergone the most deformation, and hence will show the greatest preferential orientation, consistent with the observation that the center of the inner core has a greater degree of anisotropy.

An extension to this model has been proposed by Deguen et al. (2011) using dynamic simulations, which take into account the presence of stable compositional stratification (Figure 3). Such layering concentrates the deformation into a shallow shear layer of large strain, resulting in significant deformation and textural alignment in the upper inner core; the deep inner core is less affected and preserves the textural history of the inner core.

2. Buffett and Wenk (2001) suggested, on the other hand, that the depth dependence of anisotropy can be explained by plastic deformation under the influence of electromagnetic

shear stresses (Figure 4). This would produce a toroidal-type flow, quite different from that of the previous model. Again, the high anisotropy in the lower inner core results from the fact that it is older and has had more time to develop.

3. The third possibility is that the preferred orientation was locked into the crystal on cooling from the liquid, perhaps because of flow in the outer core (Karato, 1993). If the alignment was frozen in on crystallization, there would have to be a mechanism, as yet unknown, for the formation of the outer isotropic layer. One possibility is simply that the iron phase in the outer layer of the inner core is different from that in the deeper inner core and does not have slip systems, which cause anisotropy.

The model of Yoshida et al. (1996) predicts the *c*-axis of hcp-Fe to be aligned parallel to the pole directions, while the second model of Buffett and Wenk (2001) predicts it to be in the equatorial plane. Despite the completely different underlying dynamics and the resultant flow fields, both studies were able to show that the predicted lattice preferred orientation gave an anisotropy consistent with that observed for the inner core. The reason they were able to do this was because they used different sets of elastic constants to calculate the anisotropy, and different mechanisms for producing the preferred orientation in the first place. An additional, but fundamental uncertainty in these models is that they only considered the hcp phase of iron. As shown in Section 2.06.3, there is some possibility that other phases of iron may be stable in the inner core, especially in the presence of light elements.

As well as being anisotropic and layered, the inner core exhibits a hemispherical seismic structure with an almost isotropic eastern hemisphere and a slower, more anisotropic, western hemisphere (Cao and Romanowicz, 2004; Deuss et al., 2010).

Geodynamo models suggest that thermochemical convection couples the heterogeneity of the inner core with that of the lower mantle. Circulation below Asia causes high rates of light element release in the eastern hemisphere just below the inner-core boundary (ICB), giving rise to the observed lateral seismic anomalies (Aubert et al., 2008). It has also been suggested that the origin of the hemispherical anisotropy observed by seismology is due to the dynamical motion of the inner core itself, resulting in hemispherical solidification and melting processes (Alboussière et al., 2010; Gubbins et al., 2011; Monnereau et al., 2010). It is possible that the inner core is translating eastwards, driven by convection. As it travels, it solidifies in the west because of the decrease in pressure associated with the change in the center of gravity. This solidification releases plumes enriched in lighter elements in the west, and melting in the east, resulting in a stably stratified iron-rich dense layer at the base of the outer core in the east (Figure 5). Clearly, knowledge of the physical properties that parameterize these models is essential if such models are to accurately reflect the processes occurring in Earth's core.

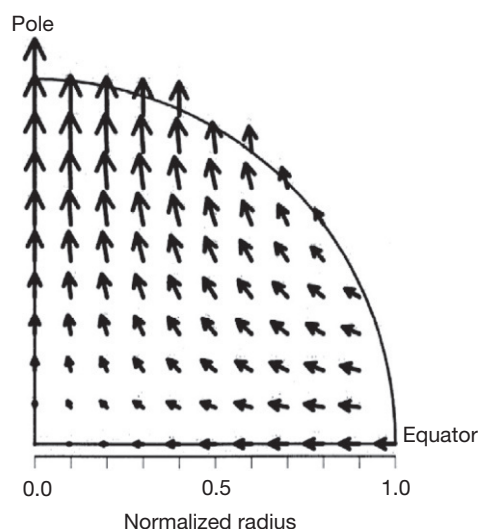


Figure 2 Flow field from Yoshida et al. (1996), showing a predominantly radial flow.

2.06.2.3 Super Rotation of the Inner Core

In addition to the core complexity mentioned earlier, there is another inference from seismology that provides a constraint on the dynamics of the inner core, in particular, inner core

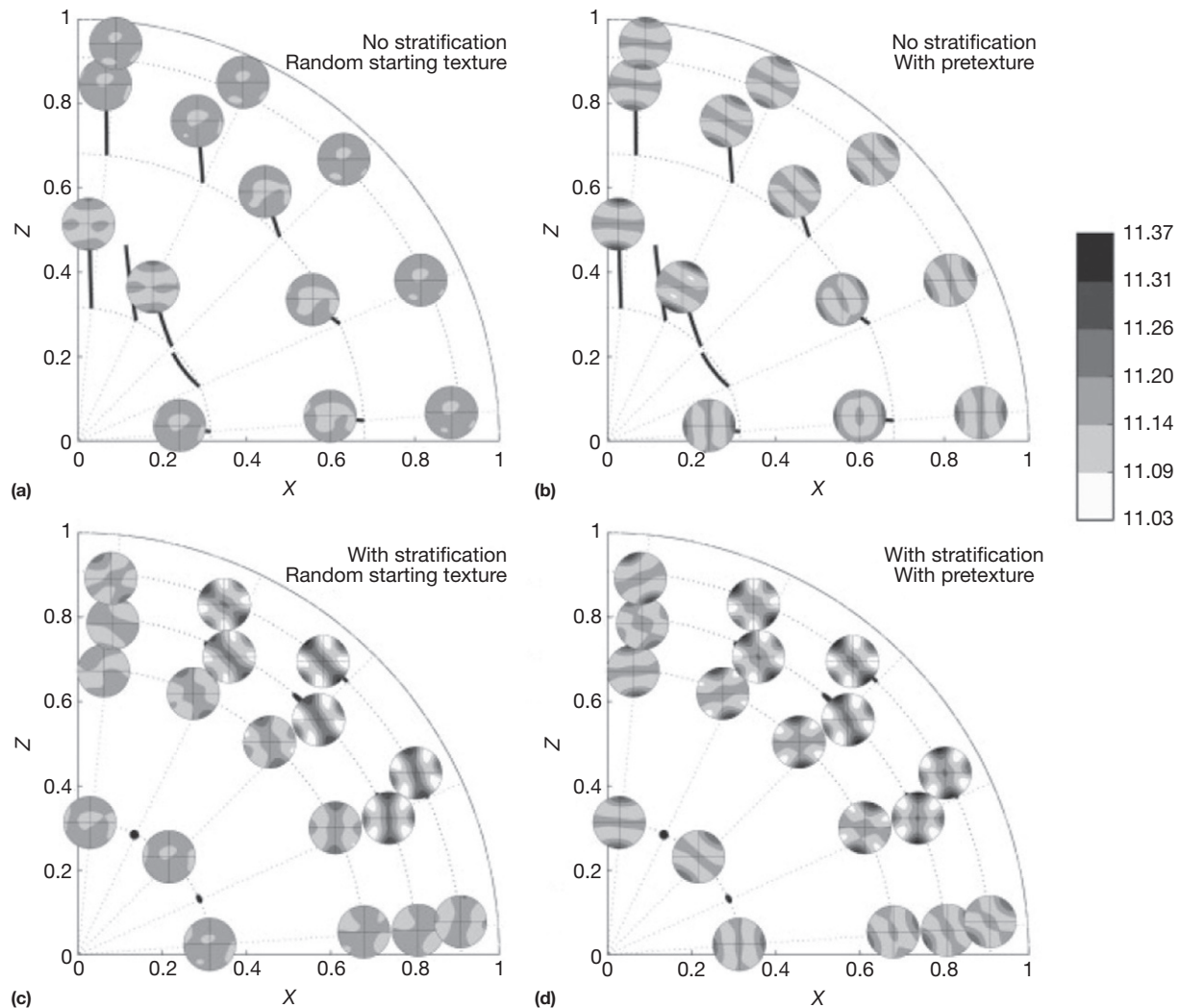


Figure 3 Present-day P-wave velocity anisotropy inside the inner core for a model with no stratification, with stratification, with a random solidification texture, and with an initial solidification texture. Velocity scale in kilometer per second. Each contour corresponds to a 0.5% change in velocity. Reproduced from Deguen R, Cardin P, Merkel S, and Lebensohn RA (2011) Texturing in Earth's inner core due to preferential growth in its equatorial belt. *Physics of the Earth and Planetary Interiors* 188: 173–184.

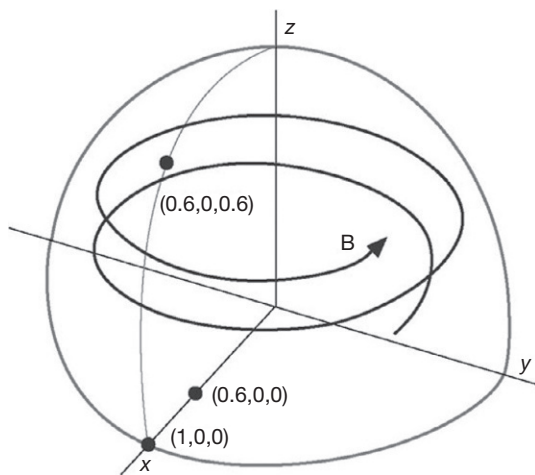


Figure 4 Direction of magnetic field causing a preferred crystal alignment in a model of Buffett and Wenk (2001).

viscosity. Seismic observations suggest that Earth's inner core may be rotating with respect to the bulk of the planet. Although there have been several seismic studies, until recently, there appeared to be no consensus as to the amount of differential rotation of Earth's core with respect to the mantle. Observations suggest rotation rates that range from marginally detectable to 3° per year (Cao et al., 2007; Collier and Helffrich, 2001; Creager, 1997; Poupinet et al., 2000; Song, 2000; Song and Li, 2000; Song and Richards, 1996; Souriau, 1998; Su et al., 1996; Tkalčić et al., 2013; Wen, 2006; Zhang et al., 2005). If the rotation rate is high, and if seismic anisotropy is due to preferred alignment, the inner core would have to adjust on a relatively short timescale in order to maintain its texture as it rotates. Collier and Helffrich (2001) suggested that the relative motion of the inner core and the mantle might take the form of an inner core oscillation on a timescale of ~ 280 days rather than a simple relative rotation of the two; this type of oscillation could be caused by the heterogeneous

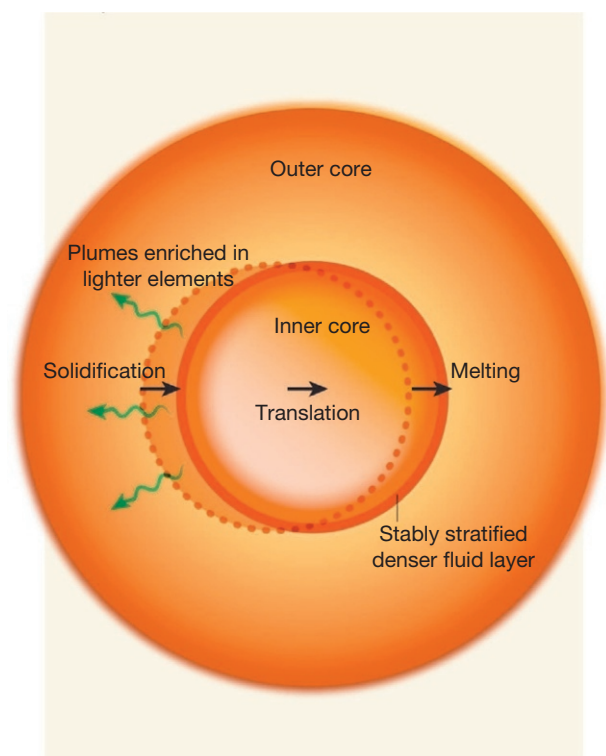


Figure 5 Alboussière et al. (2010) argue that the inner core is translating eastward, driven by convection. As it does so, it solidifies in the west, releasing plumes enriched in lighter elements, and melts in the east, resulting in an iron-enriched layer that is denser than the overlying outer core. The process of translation could also help explain the differing seismic properties between the hemispheres in the inner core. Reproduced from Bergman MI (2010) An inner core slip-sliding away. *Nature* 466: 697–698.

distribution of mass in Earth's mantle exerting a significant gravitational pull on the inner core, which will tend to keep the inner core aligned. The extent to which the inner core adjusts during differential rotation or oscillation will, therefore, depend critically on the inner core viscosity. Buffett (1997) modeled the viscous relaxation of the inner core by calculating numerically the relaxation time for the inner core to adjust, as it rotates, back to its equilibrium shape after small distortions caused by perturbations in gravitational potential imposed by the overlying mantle. He suggested that the viscosity has to be constrained to be either $< 10^{16}$ Pas or $> 10^{20}$ Pas, depending on the dynamical regime. The latter value is supported by Collier and Helffrich (2001), who concluded that the attenuation of the observed inner-core torsional oscillations with time are consistent with a viscosity of 3.9×10^{19} Pas. More recent constraints from core nutation observations put the value at 10^{14} Pas (Koot and Dumberry, 2011), while diffusion experiments at 65 GPa and 2200 K extrapolated to core conditions put the value at 10^{20} – 10^{22} Pas (Reaman et al., 2012). Clearly, an independent measure of inner core viscosity would place constraints on these values, which will depend not only on the crystal structure adopted by the iron alloy of the inner core but also on the mechanism(s) by which deformation occurs.

One major problem with relatively fast super rotation rates is that they are difficult to reconcile with the observed hemispherical seismic structure of the inner core. An inner core super rotating at 0.3 per year would take only 1000 years for a full rotation, yet a few tens of kilometers of asymmetric inner core texturing and growth are thought to require a million-year timescale. In a recent seismological study, Waszek et al. (2011) found a rotation rate of 0.1 – 1° per million years. This much slower super rotation allows for the present day hemispherical structure, explaining the previously observed faster super rotation rates in terms of large inner core fluctuations in rotation on much shorter timescales.

2.06.2.4 Seismological and Nutation Observations of the Outer Core

In general, the outer core is considered to be homogeneous because of the continual mixing of the liquid via convection. Despite this, there is some seismological evidence to suggest that there is some structure and heterogeneity in the outer core. For example, lateral velocity heterogeneities, possibly associated with the topography at the core–mantle boundary (CMB), have been observed with seismic tomography (Soldati et al., 2003). However, at present, it is impossible to be definitive as to whether or not these lateral anomalies are an artifact of the methodology (see, e.g., Lei and Zhao, 2006). There is also evidence for some structure at the top of the outer core. A very small (a few kilometers across) and thin (150 m) outer core rigidity zone may exist just below the CMB (Garnero and Jeanloz, 2000); it is possible that this anomaly is responsible for the wobbling of Earth's rotational axis (Rost and Revenaugh, 2001). Further evidence for some topography at the top of the outer core has come from observations of nutations (Buffett, 2010). In their study, the authors show that fluid stratification just below the CMB suppresses flow over the boundary topography, trapping fluid in the boundary topography; fluid below this region is well mixed within the convecting outer core (Buffett, 2010; Figure 6). Finally, there may be a mushy layer (crystals suspended in liquid) or a slurry zone (solidification via dendrites) at the base of the outer core, the latter being more likely (Shimizu et al., 2005); such a layer is supported by seismic observations (Zou et al., 2008).

2.06.3 The Structure and Anisotropy of Iron in the Inner Core

Accurate mineral physics data can be used to resolve many of the uncertainties regarding the structure and composition of Earth's core; however, as mentioned in Section 2.06.1, the mineralogical model that comes out of combining theoretical and experimental studies must match the seismological observations exactly. Furthermore, the seismological observations themselves must be sufficiently detailed and robust to enable accurate and meaningful comparisons to be made. To a first approximation, Earth's core is made of iron and, therefore, if we are to understand Earth's core, we must first understand how iron behaves under core pressures and temperatures.

The properties of the inner core are determined by the materials present; although we know that the inner core is

made of iron alloyed with nickel and other lighter elements (see [Section 2.06.8](#)), we must first understand the behavior of pure iron before we are able to understand the behavior of more complex iron alloys. However, the properties of pure

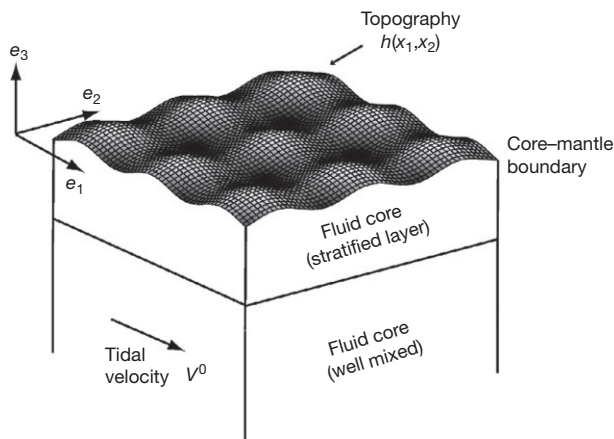


Figure 6 Schematic illustration of the core-mantle boundary (CMB) region. A stable stratification occurs in a thin layer below the CMB, and the deeper fluid is well mixed by convection. Tidal motions in the well-mixed region drive flow in the overlying stratified layer, but the fluid closest to the CMB is trapped by the boundary topography. Shear flow develops within the stratified layer, generating electric currents in the presence of a vertical magnetic field. Reproduced from Buffett BA (2010) Chemical stratification at the top of Earth's core: Constraints from observations of nutations. *Earth and Planetary Science Letters* 296: 367–372.

iron relevant to Earth's core depend upon the structure iron adopts at core conditions, and it is this issue we need to address first.

Experimentalists have put in an enormous effort over the last 25 years into obtaining a phase diagram of pure iron, but above relatively modest pressures and temperatures, there has, until recently, been much uncertainty ([Brown, 2001](#)). Under ambient conditions, Fe adopts a bcc structure that transforms with temperature to a fcc form, and with pressure to an hcp phase, ϵ -Fe. The high-P/T phase diagram of pure iron itself, however, has been controversial (see [Figure 7](#) and also the discussion in [Stixrude and Brown \(1998\)](#)). Various diamond anvil cell (DAC)-based studies have been interpreted as showing that hcp-Fe transforms at high temperatures to a phase that has variously been described as having a double hcp structure ([Saxena et al., 1996](#)) or an orthorhombically distorted hcp structure ([Andrault et al., 1997](#)). Furthermore, high-pressure shock experiments have also been interpreted as showing a high-pressure solid-solid phase transformation ([Brown, 2001](#); [Brown and McQueen, 1986](#)), which has been suggested to be caused by the development of a bcc phase ([Matsui and Anderson, 1997](#)). Other experimentalists, however, have failed to detect such a post-hcp phase (e.g., [Nguyen and Holmes, 2004](#); [Shen et al., 1998](#)), and have suggested that the previous observations were due either to minor impurities or to metastable strain-induced behavior. Finally, recent experiments by [Tateno et al. \(2010\)](#), confirmed by [Sakai et al. \(2011\)](#), make the now growing consensus that pure iron would exist in the hcp phase at the simultaneous pressures and temperatures of Earth's inner core ([Figure 8](#)) more convincing.

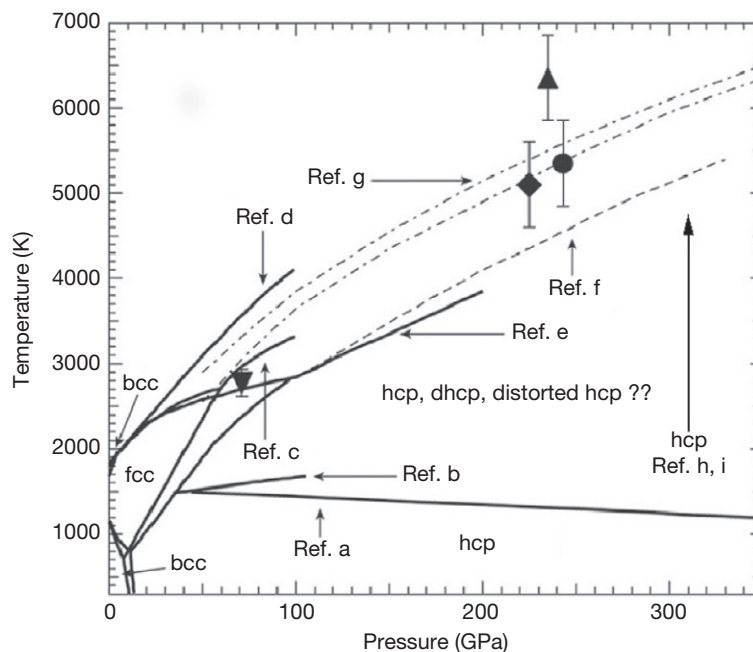


Figure 7 Phase diagram of pure iron (adapted from [Nguyen JH and Holmes NC \(2004\)](#) Melting of iron at the physical conditions of the Earth's core. *Nature* 427: 339–342). Solid lines represent phase boundaries and melt lines from DAC experiments; symbols with error bars are points on the melting curve from shock experiments; broken lines are melting curves from first-principles calculations. DAC data: Ref. a: [Saxena and Dubrovinsky \(2000\)](#); b: [Andrault et al. \(2000\)](#); c: [Shen et al. \(1998\)](#); d: [Williams et al. \(1987\)](#); e: [Boehler \(1993\)](#). Shock data: triangle: [Yoo et al. \(1993\)](#); circles: [Brown and McQueen \(1986\)](#); reverse triangle: [Ahrens et al. \(2002\)](#); diamond: [Nguyen and Holmes \(2004\)](#). First-principles calculations: f: [Laio et al. \(2000\)](#); g: [Alfè et al. \(2002b\)](#); h: [Vočadlo et al. \(2000a\)](#); i: [Vočadlo et al. \(2003a\)](#).

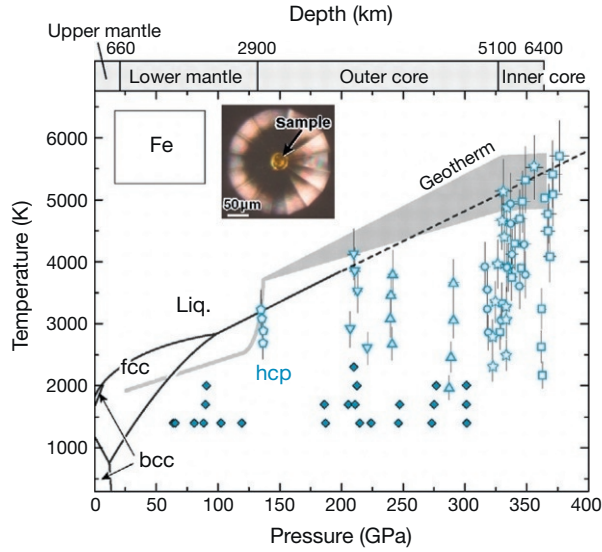


Figure 8 Phase diagram of Fe and the inferred temperature profile inside Earth. Open symbols indicate the results from Tateno et al (2010) – different symbols indicate different runs, and solid diamonds indicate data from previous experimental work (Kuwayama et al., 2008). Inset: sample photograph at 335 GPa in the DAC. Reproduced from Tateno S, Hirose K, Ohishi Y, and Tatsumi Y (2010) The structure of iron in Earth's inner core. *Science* 330: 359–361.

Theoretical computer calculations of the static, zero-Kelvin solid (Stixrude et al., 1997; Vočadlo et al., 2000a) suggested that the hcp phase of iron is likely the most stable phase at inner core pressures. The bcc phase of iron was considered an unlikely candidate for a core-forming phase because it is elastically unstable at high pressures (and 0 K), with an enthalpy considerably higher than that of hcp-Fe (Söderlind et al., 1996; Stixrude and Cohen, 1995a; Vočadlo et al., 2000a). At core pressures, the bcc phase is also vibrationally unstable (Söderlind et al., 1996; Stixrude and Cohen, 1995b; Vočadlo et al., 2003a; Figure 9). However, ab initio molecular dynamics calculations at simultaneously high pressures and temperatures have found that the bcc phase of iron becomes entropically stabilized by temperature (Vočadlo et al., 2003a), but remains unstable with respect to tetragonal strain (Vočadlo et al., 2008b). The free energies of the bcc, hcp, and fcc phases have been calculated (Vočadlo et al., 2003a, 2008a,b) and the results show that, although the free energy of the hcp phase is the lowest, the free energy differences are very small (a few meV per atom at a density of $13\,155\text{ kg m}^{-3}$ and a temperature of 5500 K). Further calculations of the fcc phase (Côté et al., 2012; Mikhaylushkin et al., 2007) at core pressures and temperatures show that this phase becomes increasingly stable with temperature ($>6000\text{ K}$). In contrast, recent first-principles calculations by Stixrude (2012) show a much wider stability field of hcp to 2300 GPa and 19 000 K (Figure 10). It is clear that, although the stable phase

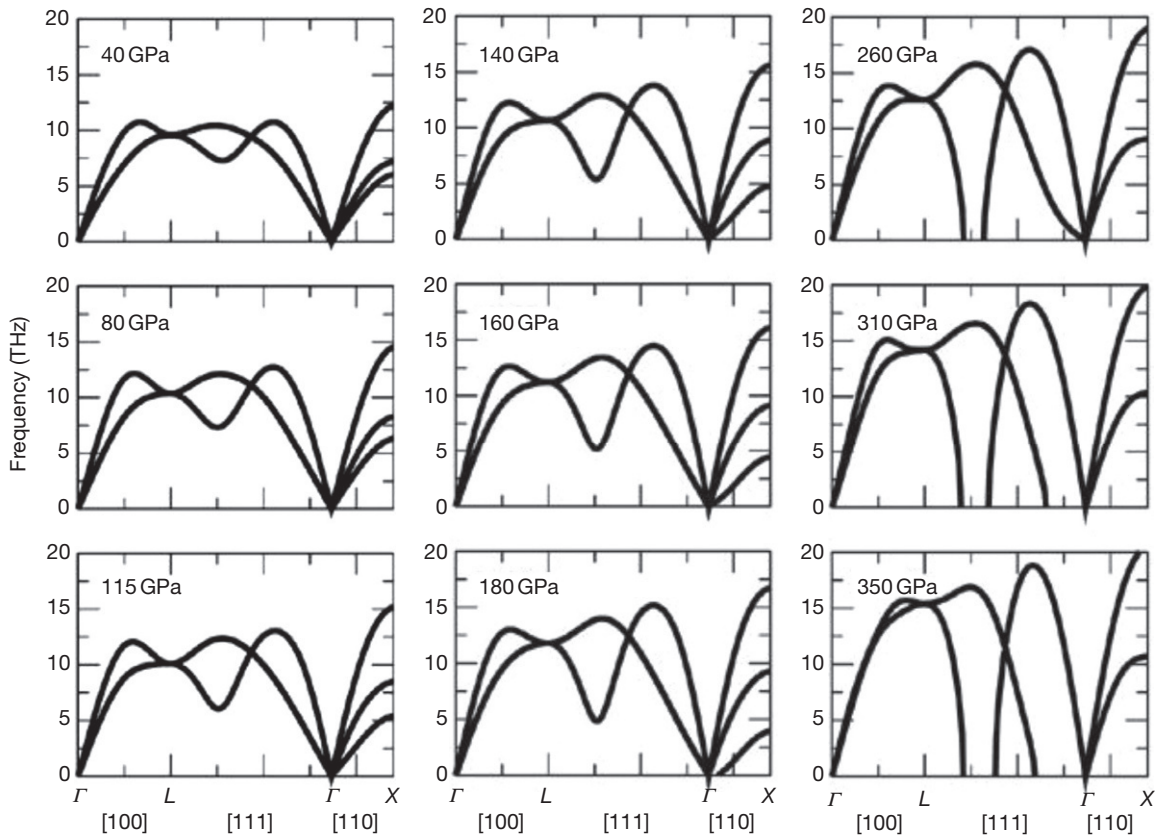


Figure 9 The calculated phonon dispersion curves for bcc-Fe at nine different volumes (corresponding to ~40–350 GPa) (Vočadlo et al., 2003a). The softening in the [110] direction at ~180 GPa indicates the onset of the bcc to fcc transition, and that in the [111] direction above ~260 GPa corresponds to the bcc to ω transition.

of pure iron at core conditions is hcp-Fe, the small free energy differences between the phases, together with the presence of light elements, mean that both fcc-Fe and bcc-Fe cannot be ruled out as an inner core phase.

In summary, therefore, based on experiments at core conditions (Sakai et al., 2011; Tateno et al., 2010) and ab initio calculations (Stixrude, 2012; Vočadlo et al., 2003a,b, 2008a,b), the stable phase of pure iron at core conditions is almost

certainly the hcp phase. However, the free energies of hcp-, bcc-, and fcc-Fe are almost identical (within ~ 35 meV $\cdot$ atom $^{-1}$), only marginally favoring hcp-Fe. As a result of these small free energy differences, the relative phase stability may be greatly affected by the presence of alloying elements that are known to exist in the inner core.

2.06.4 Thermoelastic Properties of Solid Iron

The only experimental data on solid iron under true core pressures and temperatures comes from either simultaneously high-P/high-T static experiments or shock experiments; however, although the measurement of temperature in shock experiments has been attempted, it is problematic (e.g., Yoo et al., 1993). There are a number of static experimental studies on pure iron at ambient pressures and high temperatures, and high pressures and ambient temperatures (see later). Simultaneously high-pressure/high-temperature experiments are very challenging, although they have been attempted (e.g., the iron phase diagram given earlier). In this section, we look at the thermoelastic properties of iron as obtained from ab initio calculations, and, where available, experimental data.

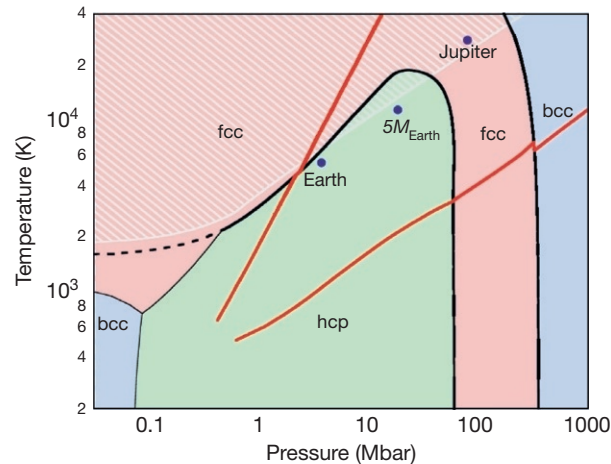


Figure 10 Phase diagram of iron to extreme pressures, taken from Stixrude (2012). Bold black lines are results from Stixrude (2012); thin black lines show experimental phase boundaries. Red lines are the calculated isentropes (lower) and Hugoniot (upper). The black-dashed line is the low pressure fcc–hcp boundary where magnetic ordering has been neglected. The stability field of the liquid is shown by the gray section and is estimated from Lindemann’s law using the calculated vibrational frequencies. Reproduced from Stixrude L (2012) Structure of iron to 1 Gbar and 40,000 K. *Physical Review Letters* 108: 055505.

2.06.4.1 Equation of State

The equation of state for hcp-Fe has been studied both experimentally (e.g., Brown and McQueen, 1986; Mao et al., 1990) and computationally (e.g., Söderlind et al., 1996). In Figure 11, we show the density as a function of pressure from ab initio calculations together with that from static compression measurements at 300 K (Mao et al., 1990), shock experiments (Brown and McQueen, 1986), theoretical calculations (Steinle-Neumann et al., 2002; Stixrude et al., 1997), and an

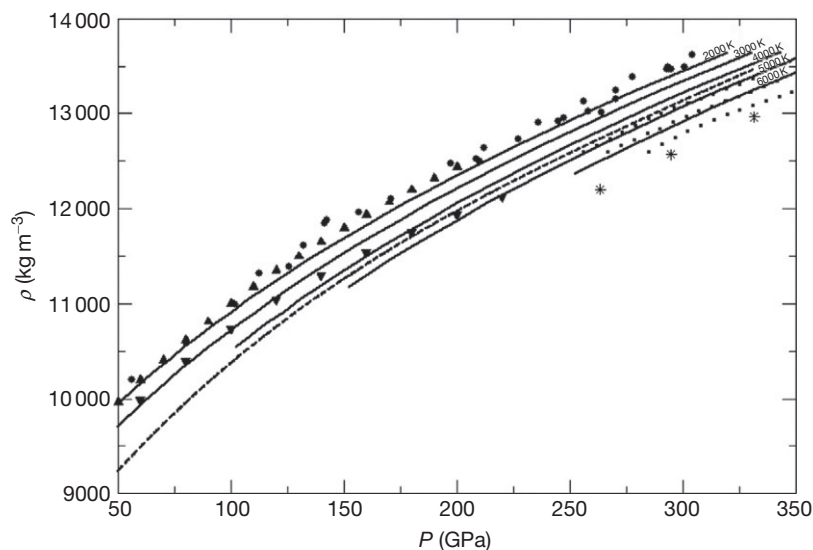


Figure 11 Density as a function of pressure for hcp-Fe from ab initio calculations along isotherms between 2000 and 6000 K (modified from Vočadlo L, Alfe D, Gillan MJ, Wood IG, Brodholt JP, and Price GD (2003b) Possible thermal and chemical stabilisation of body-centred-cubic iron in the Earth’s core. *Nature* 424: 536–539). Filled circles are the static compression measurements at 300 K (Mao et al., 1990); dashed line is the calculation for the 4000 K isotherm of Stixrude et al. (1997); dotted lines are the 5000, 6000, and 7000 K isotherms of Steinle-Neumann et al., 2002; stars are from an analysis of a thermal equation of state at 6000 K (Isaak and Anderson, 2003); triangles up and down are the experiments of Brown and McQueen (1986) along the 300 K isotherm and Hugoniot, respectively.

analysis at 6000 K based on a thermal equation of state (Isaak and Anderson, 2003). All the results from both theory and experiment are in comforting agreement and provide a successful basis from which to make further comparisons of other properties.

2.06.4.2 Incompressibility

The isothermal and adiabatic incompressibility (K_T and K_S , respectively) are shown in Figure 12. The incompressibility increases significantly (and almost linearly) with pressure, and decreases with increasing temperature (more so in the case of K_T than K_S).

2.06.4.3 Thermal Expansion

The thermal expansivity, α , determined by ab initio computer calculations (Vočadlo et al., 2003b), is shown in Figure 13 together with the value determined from shock data at 5200 K (Duffy and Ahrens, 1993), the theoretical calculations of Stixrude et al. (1997), and an analysis using a thermal equation of state (Anderson and Isaak, 2002; Isaak and Anderson, 2003). It is clear that α decreases strongly with increasing pressure and increases significantly with temperature.

2.06.4.4 Elasticity of Solid Iron

A fundamental step toward resolving the structure and composition of Earth's inner core is to obtain the elastic properties of the candidate phases that could be present.

2.06.4.4.1 Elastic constants of iron as a function of pressure at zero Kelvin

The elastic constants of hcp-Fe at 39 and 211 GPa and ambient temperature have been measured experimentally (Mao et al., 1999). Calculations of elastic constants at 0 K for hcp-Fe have

been reported by Stixrude and Cohen (1995a), Söderlind et al. (1996), Steinle-Neumann et al. (1999), and Vočadlo et al. (2003b). These values are plotted as a function of density in Figure 14(a) and 14(b). Although there is some scatter on the reported values of c_{12} , overall the agreement between the experimental and various ab initio studies is excellent.

The resulting bulk and shear moduli and the seismic velocities of hcp-Fe as a function of pressure are shown in Figures 15 and 16, along with the experimental data. The calculated values compare well with the experimental data at higher pressures; the discrepancies at lower pressures are probably due to the neglect of magnetic effects in the simulations (see Steinle-Neumann et al., 1999).

2.06.4.4.2 High-temperature elastic behavior and wave velocities

The high-temperature elastic behavior of iron can be estimated by considering Birch's law, which suggests that a linear relationship exists between the bulk sound speed, V_Φ , and density, ρ ; in the absence of reliable experimental data at very high pressures and temperatures, it has been assumed that this linearity may be extrapolated to the conditions of the inner core. Badro et al. (2007) used inelastic x-ray scattering in a DAC at high pressures, but ambient temperatures, to demonstrate a linear relationship between V_p and ρ for a number of systems including hcp-Fe. Figure 17 shows the fit to their results extrapolated to core density, together with the results from Vočadlo (2007) (where the uncertainties lie within the symbols) and also the results from shock experiments (Brown and McQueen, 1986). The agreement is generally very good; it is noteworthy that the calculated bcc-Fe and hcp-Fe velocity-density systematics are indistinguishable.

More recent experimental data up to 93 GPa and 1100 K (Antonangeli et al., 2012) confirm the equivalence of temperature and density via Birch's law as V_p scales linearly with density (Figure 18).

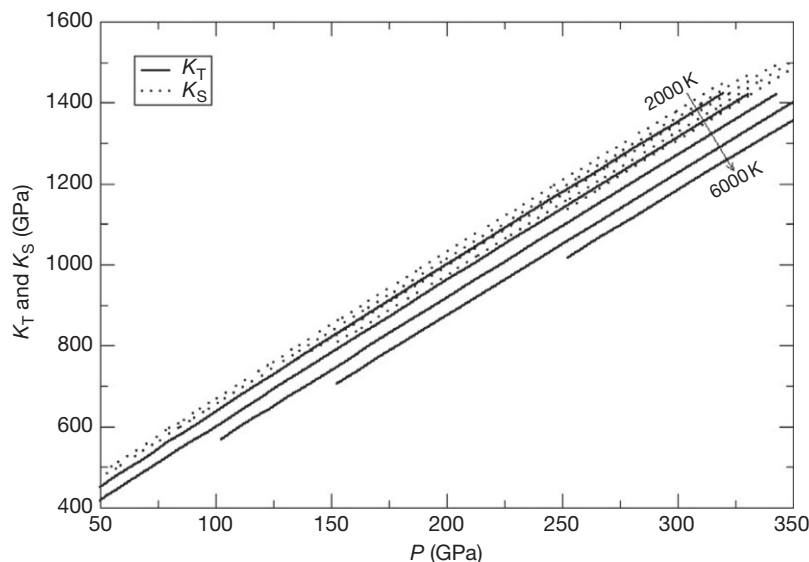


Figure 12 Isothermal incompressibility, K_T (solid lines), and adiabatic incompressibility, K_S (dotted lines), as a function of pressure for hcp-Fe from ab initio calculations along isotherms between 2000 and 6000 K. Reproduced from Vočadlo L, Alfe D, Gillan MJ, Wood IG, Brodholt JP, and Price GD (2003b) Possible thermal and chemical stabilisation of body-centred-cubic iron in the Earth's core. *Nature* 424: 536–539

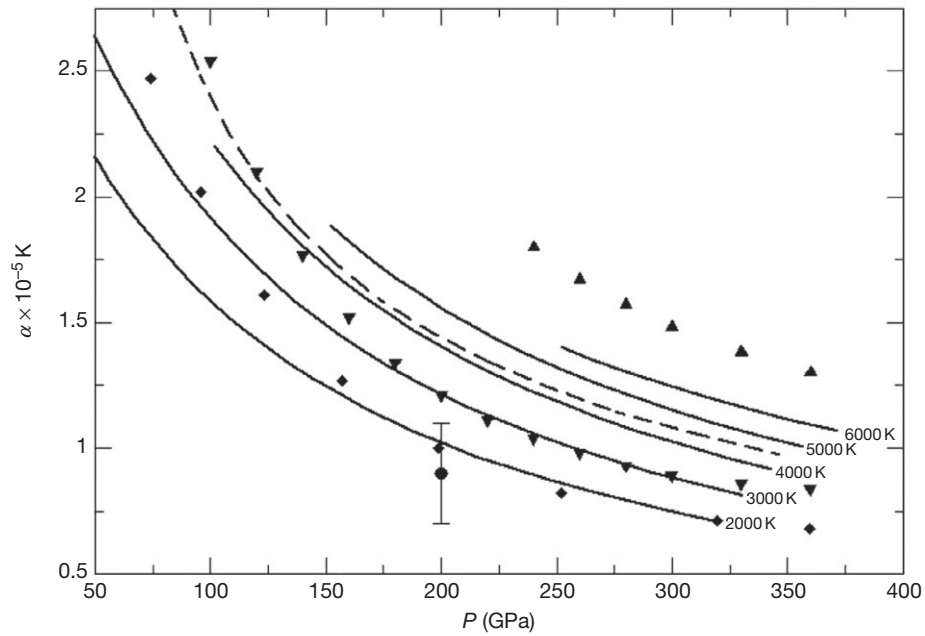


Figure 13 Thermal expansion as a function of pressure for hcp-Fe from ab initio calculations (Vočadlo et al., 2003b) along isotherms between 2000 and 6000 K (solid lines). The circle is the value of Duffy and Ahrens (1993) determined from shock experiments at 5200 ± 500 K; the dashed line is from theoretical calculations for the 4000 K isotherm (Stixrude et al., 1997); the diamonds are from an analysis of room temperature compression data at 300 K (Anderson and Isaak, 2002); the triangles (up: 6000 K, down: 2000 K) are from an analysis using a thermal equation of state applied to room temperature compression data (Isaak and Anderson, 2003). Modified from Vočadlo L, Alfe D, Gillan MJ, Wood IG, Brodholt JP, and Price GD (2003b) Possible thermal and chemical stabilisation of body-centred-cubic iron in the Earth's core. *Nature* 424: 536–539.

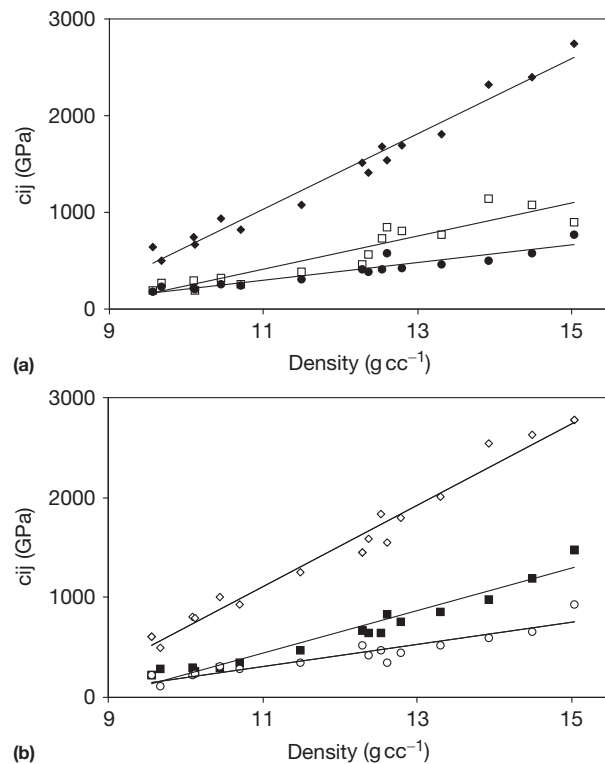


Figure 14 Combined plot of the elastic constants of hcp-Fe as a function of density calculated at 0 K from Stixrude and Cohen (1995b), Söderlind et al (1996), Steinle-Neumann et al. (1999), and Vočadlo et al. (2003b) together with the experimental values of Mao et al. (1999); (a) c_{11} black diamonds, c_{12} white squares, c_{44} black circles, (b) c_{33} white diamonds, c_{13} black squares, and c_{66} white circles.

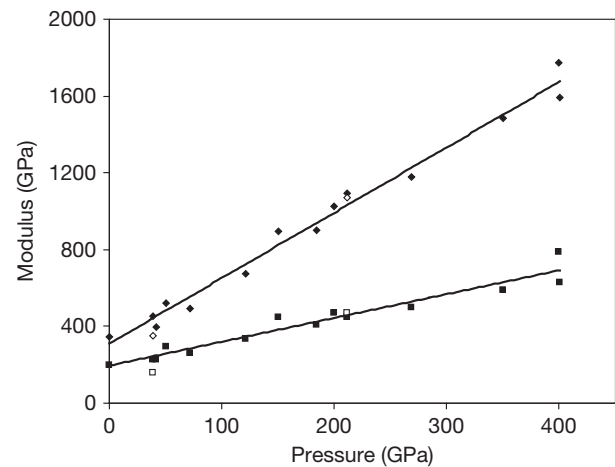


Figure 15 Plot of bulk modulus (diamonds) and shear modulus (squares) for hcp-Fe as a function of pressure, with values taken from Stixrude and Cohen (1995a), Steinle-Neumann et al. (1999), Söderlind et al. (1996), Mao et al. (1999), and Vočadlo et al. (2003b). Black diamonds and squares represent ab initio values, while white diamonds and squares represent values obtained from experimentally determined elastic constants.

Figure 19 shows how V_Φ varies with density for both athermal and high-temperature (up to 5500 K) ab initio calculations (Vočadlo, 2007), together with values from PREM (Dziewonski and Anderson, 1981), from the experiments of Brown and McQueen (1986), and from a previous computational study (6000 K; Steinle-Neumann et al., 2001). It is clear that Birch's law holds for iron and that the velocities at constant density are almost temperature-independent.

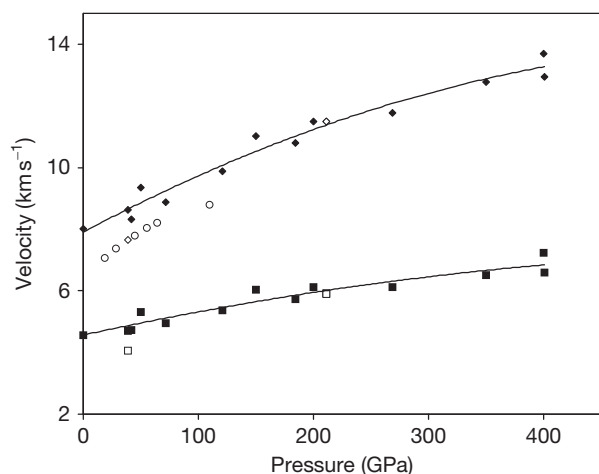


Figure 16 Plot of aggregate V_P (diamonds) and V_S (squares) wave velocity for hcp-Fe as a function of pressure, with values taken from Stixrude and Cohen (1995a), Steinle-Neumann et al. (1999), Söderlind et al. (1996), Mao et al. (1999), and Vočadlo et al. (2003b). Black diamonds and squares represent ab initio values, while white diamonds and squares represent values obtained from experimentally determined elastic constants. White circles are the experimental data of Fiquet et al. (2001).

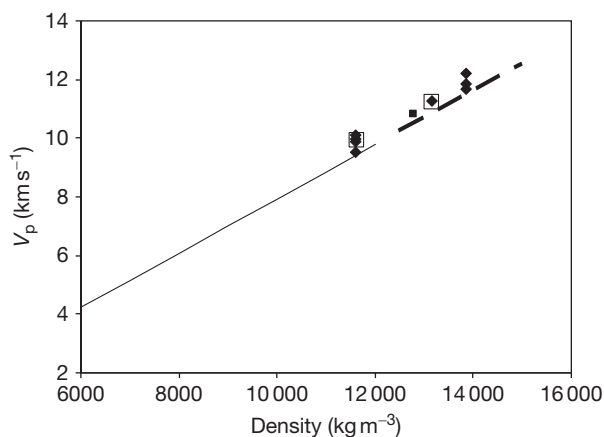


Figure 17 P-wave velocity as a function of density for pure iron compared with the high-P ambient-T DAC experiments of Badro et al. (2007); solid line is the fit to data, dashed line is an extrapolation of the fit. Diamonds: calculated bcc-Fe V_P at different temperatures; open squares: calculated hcp-Fe at different temperatures (Vočadlo, 2007); filled square: shock experiments of Brown and McQueen (1986).

2.06.4.4.3 P-wave anisotropy

As discussed in Section 2.06.2.2, seismic observations show that the P-wave velocity through the inner core is 3–5% faster in the polar direction than in the equatorial plane (e.g., Song and Helmberger, 1998). Experiments at moderate pressure and ambient temperature (Antonangeli et al., 2004), and calculations (Stixrude and Cohen, 1995a) at high pressures but at 0 K, showed that the compressional wave velocity along the c -axis of hcp-Fe is significantly faster than that in the basal plane; this led to the conclusion that the inner core is made up of oriented hcp-Fe crystals with the c -axis parallel to the rotational axis (Figure 20). However, more recent calculations (using a particle-in-cell method) found that the elastic properties of

hcp-Fe change dramatically as a function of temperature (Steinle-Neumann et al., 2001; Figure 21), and that compressional waves travel faster in the basal plane of hcp-Fe at high temperatures and pressures, in complete contrast to the low temperature results; this effect was also seen in ab initio molecular dynamics calculations (Vočadlo et al., 2009; Figures 22 and 23). The sense of the anisotropy is such that V_P is fastest along the c -axis up to 5000 K but becomes reversed by 5500 K, with V_P then becoming faster in the a - b plane. These results can account for the observed overall seismic anisotropy if the preferred orientation of hcp-Fe in the inner core is with the c -axis aligned parallel to the equatorial plane instead of parallel to the poles. Obviously, if the seismic anisotropy is caused by deformation, the three studies imply very different stresses and flow fields in the inner core (as described in Section 2.06.2.2). Indeed, for an iron core dominated by aligned crystals of hcp-Fe, with the c -axis aligned in the polar direction, the seismically observed isotropic outer-inner core could result from hcp-Fe close to melting where axial wave velocities become similar, while at greater depths, where iron is further from the melting point, a greater anisotropy can be achieved. A more recent study, however, shows that at the pressures of the center of the inner core (360 GPa) as opposed to the pressures required to produce inner core density (316 GPa) and high temperatures (just before melting), no c_{11} – c_{33} crossover occurs and the sense of P-wave anisotropy is always such that the fast direction is along the c -axis (Figure 24; Martorell et al., 2013b). This work also shows significant shear softening as the melting temperature is approached.

Figure 25 shows the P-wave anisotropy from ab initio molecular dynamics calculations of hcp-Fe compared to that for fcc-Fe and bcc-Fe at 316 GPa and 5500 K. For fcc-Fe, the maximum anisotropy along mutually perpendicular directions is 6% for crystals aligned along $\langle 100 \rangle$. For bcc-Fe, the maximum anisotropy that can be achieved through mutually perpendicular directions is never more than $\sim 2\%$. For the hcp-Fe phase, an $\sim 3\%$ anisotropy can be achieved through mutually perpendicular directions whereby, for the polar P-wave velocity to be faster, the c -axis of the crystals would lie in Earth's equatorial plane; this is close to the experimentally determined value of 4–5% (Antonangeli et al., 2004). Thus, for the bcc phase of iron, the observed seismic anisotropy in Earth's inner core cannot be achieved by alignment alone, while for the hcp and fcc phases, it is just possible to achieve the required degree of anisotropy but only by a significant crystalline alignment. Such a high degree of alignment may not be necessary if the seismically observed P-wave anisotropy does not strictly require mutually perpendicular directions.

2.06.4.4.4 Shear-wave anisotropy of the inner core

While currently very difficult to detect, shear-wave anisotropy in the inner core has been observed in a number of seismic studies. PKJKP data suggest that shear-wave anisotropy increases with depth (Cao and Romanowicz, 2009) and can be modeled by alignment of hcp-Fe crystals with the c -axis perpendicular to the rotational axis, while normal mode studies reveal an upper layer in the inner core (Irving and Deuss, 2011) in which the shear-wave velocity is isotropic. Experimental studies on textured hcp-Fe at pressures up to 172 GPa show that V_S is 2–4% faster along the c -axis than the a -axis (Lin et al., 2010), while theoretical studies on the bcc, fcc, and hcp phases of iron find the

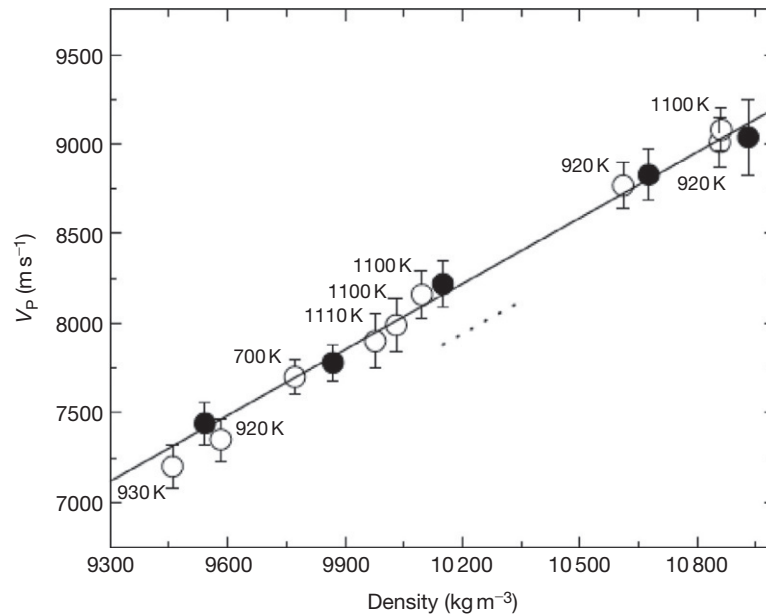


Figure 18 Aggregate compressional wave velocity measured at ambient temperature (solid symbols) and high temperature (open symbols) plotted as a function of density. The dotted line is the velocity reduction expected at 1100 K for a softening of $0.35 \text{ ms}^{-1} \text{ K}^{-1}$ at a constant density of 10250 kg m^{-3} . Reproduced from Antonangeli D, et al. (2012) Simultaneous sound velocity and density measurements of hcp iron up to 93 GPa and 1100 K: An experimental test of the Birch's law at high temperature. *Earth and Planetary Science Letters* 331: 210–214.

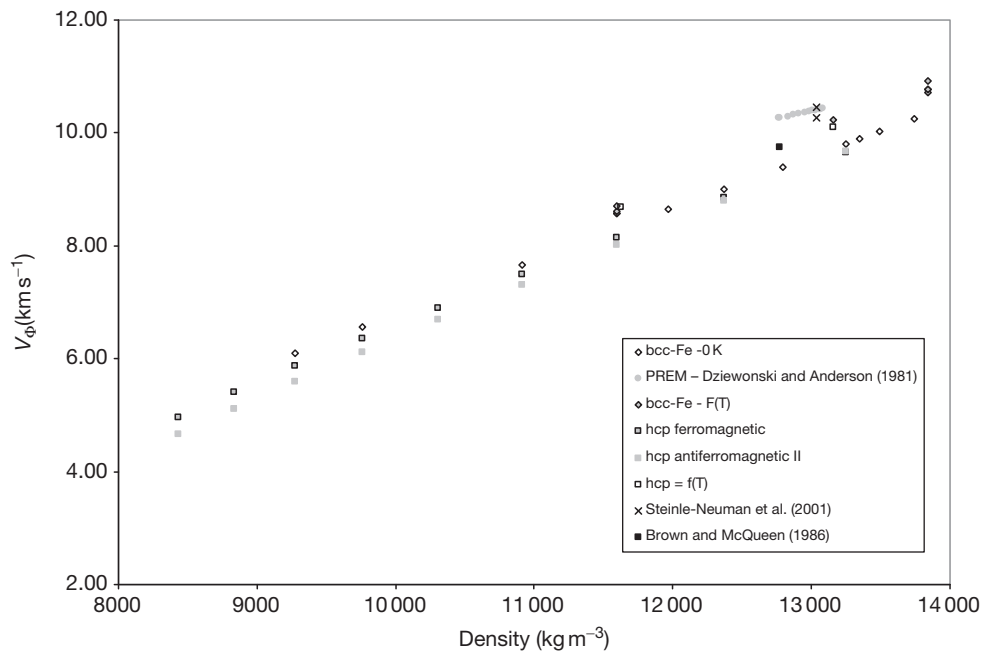


Figure 19 Calculated bulk sound velocity as a function of density for pure iron (Vočadlo, 2007) compared with previous calculations (Steinle-Neumann et al., 2001), PREM (Dziewonski and Anderson, 1981) and the shock experiments of Brown and McQueen (1986).

maximum shear-wave anisotropy at $\sim 316 \text{ GPa}$ and $\sim 5500 \text{ K}$ to be considerably higher (20%, 80% and 26%, respectively; Vočadlo et al., 2008a). In contrast, using a different methodology, more recent calculations find that hcp-Fe becomes increasingly isotropic in both V_P and V_S with temperature, to the extent that, by the time Earth's core conditions are reached, iron is elastically isotropic (Sha and Cohen, 2010).

The seismically observed anisotropy and layering in the inner core could, therefore, be accounted for if the iron crystals (of single or mixed phases) were randomly oriented in the isotropic upper layer and significantly aligned in the anisotropic lower layer. In order to draw any further conclusions about the elasticity of the inner core, however, the effect of light elements must first be taken into account (see Section 2.06.8.3).

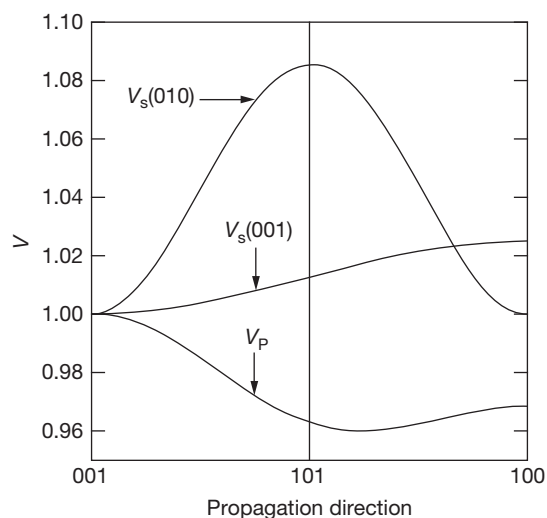


Figure 20 Single-crystal velocities in hcp-Fe as a function of propagation direction with respect to the c -axis. Note that $V_p(90^\circ) < V_p(0^\circ)$. Reproduced from Stixrude L and Cohen RE (1995) High pressure elasticity of iron and anisotropy of Earth's inner core. *Science* 267: 1972–1975.

2.06.5 The Temperature in Earth's Core

Having shown how mineral physics can be used to understand the properties of solid iron, we turn now to its melting behavior. An accurate knowledge of the melting properties of Fe is particularly important, as the temperature distribution in the core is relatively uncertain and a reliable estimate of the melting temperature of Fe at the pressure of the ICB would impose a much-needed constraint on core temperatures. As with the subsolidus behavior of Fe, there is much controversy over its high- P melting behavior. Static compression measurements of the melting temperature, T_m , have been made up to ~ 200 GPa with the DAC (e.g., [Boehler, 1993](#)) and, more recently, using a laser-heated fast x-ray diffraction technique, which provides an unambiguous signature of melting ([Anzellini et al., 2013](#); [Figure 26](#)), but even at lower pressures, results for T_m disagree by several hundred Kelvin. Shock experiments are at present the only available method to determine melting at inner core pressures, but their interpretation is not simple, and there is a scatter of at least 2000 K in the reported T_m of Fe at ICB pressures (see [Nguyen and Holmes, 2004](#)).

An alternative to experiment is theoretical calculations, which can, in principle, determine accurate melting curves to any desired pressure. Indeed, ab initio methods have successfully been used to calculate the melting behavior of transition metals such as aluminum ([Vočadlo and Alfe, 2002](#)) and copper ([Vočadlo et al., 2004](#)). Using the technique of thermodynamic integration, [Alfe et al. \(1999, 2004\)](#) calculated the melting curve of iron. The condition for two phases to be in thermal equilibrium at a given temperature, T , and pressure, P , is that their Gibbs free energies, $G(P, T)$, should be equal. To determine T_m at any pressure, therefore, [Alfe et al. \(1999, 2004\)](#) calculated G for the solid (hcp) and liquid phases of iron as a function of T and determined where they are equal. In the more recent simulations, [Alfe et al. \(2004\)](#) obtained an estimate of T_m of Fe at ICB

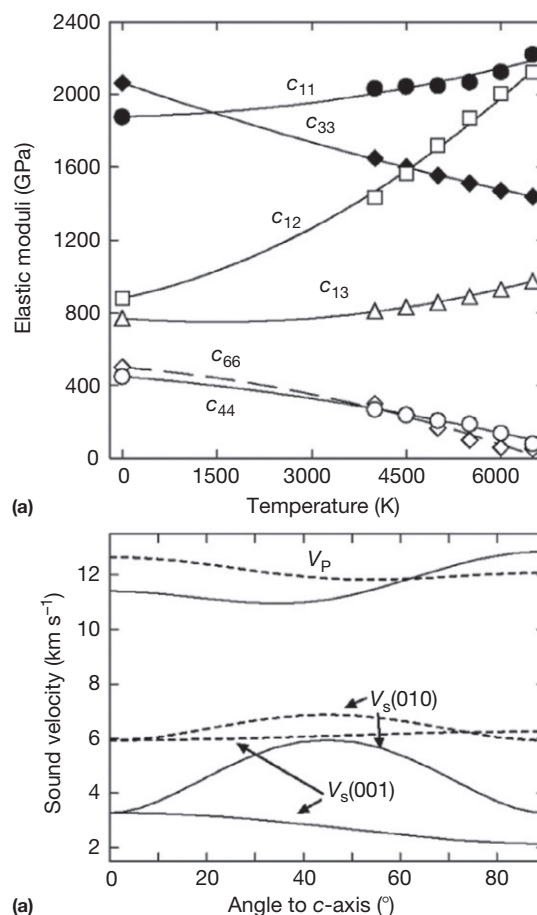


Figure 21 (a) Single-crystal elastic constants as a function of temperature. Note the marked reductions in c_{33} , c_{44} , and c_{66} . (b) Single-crystal velocities in hcp-Fe as a function of propagation direction with respect to the c -axis. Results at 6000 K (solid lines) are compared to static results (dashed lines). Note that at 6000 K, $V_p(90^\circ) > V_p(0^\circ)$. Reproduced from Steinle-Neumann G, Stixrude L, Cohen RE, and Gulseren O (2001) Elasticity of iron at the temperature of the Earth's inner core. *Nature* 413: 57–60.

pressures to be ~ 6250 , with an error of ± 300 K. For pressures $P < 200$ GPa (the range covered by DAC experiments), their curve lies ~ 900 K above the values of [Boehler \(1993\)](#) and ~ 200 K above the more recent values of [Shen et al. \(1998\)](#) (who stress that their values are only a lower bound to T_m). The ab initio curve falls significantly below the shock-based estimates for the T_m of [Yoo et al. \(1993\)](#), in whose experiments temperature was deduced by measuring optical emission (however, the difficulties of obtaining temperature by this method in shock experiments are well known), but accords almost exactly with the shock data value of [Brown and McQueen \(1986\)](#) and the data of [Nguyen and Holmes \(2004\)](#), and is in identical agreement with the most recent experimental estimate of 6230 ± 500 K ([Anzellini et al., 2013](#); [Figure 26](#)). The ab initio melting curve of [Alfe et al. \(2004, 2009\)](#) differs somewhat from the calculations of both [Belonoshko et al. \(2000\)](#) and [Laio et al. \(2000\)](#). However, the latter two authors used model potentials fitted to ab initio simulations, and so their melting curves are those of the model potential and not the true ab initio one (it is

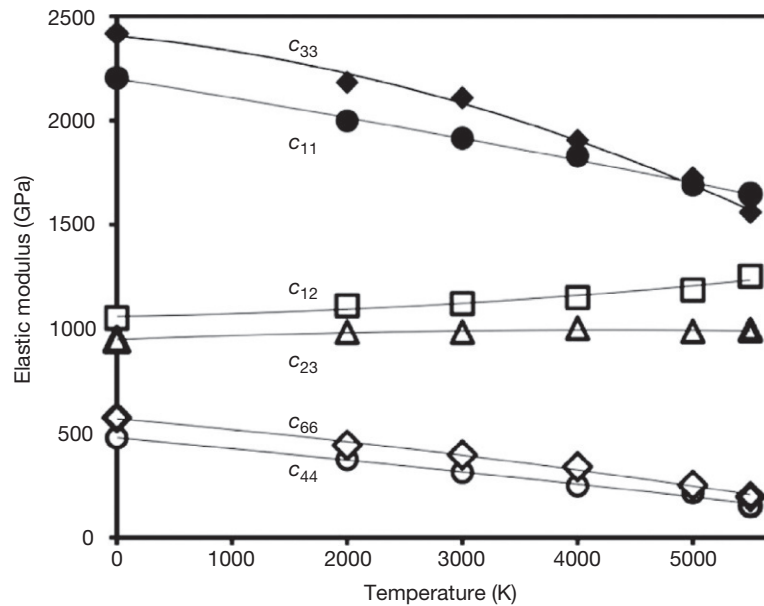


Figure 22 Elastic constants of hcp-Fe at 316 GPa as a function of temperature; c_{66} is not independent and is equal to $1/2(c_{11} - c_{12})$. Those at 5500 K are taken from earlier work (Vočadlo, 2007). Reproduced from Vočadlo L, Dobson D, and Wood IG (2009) Ab initio calculations of the elasticity of hcp-Fe as a function of temperature at inner-core pressure. *Earth and Planetary Science Letters* 288: 534–538.

important to note here that Laio et al. (2000) used a more sophisticated approach in which the model potential had an explicit dependence on the thermodynamic state that exactly matched the ab initio result). In their paper, Alfè et al. (2004) illustrated this ambiguity by correcting for the errors associated with the potential fitting of Belonoshko et al. (2000); the result is in almost exact agreement with the true ab initio curve. Finally, using quantum Monte Carlo techniques to compute the free energies of solid and liquid iron at ICB conditions, Sola and Alfè (2009) obtained a significantly higher iron melting temperature at 330 GPa of 6900 ± 400 K.

The addition of light elements is estimated to reduce the melting temperature of pure iron by ~ 700 K making the likely temperature at the ICB somewhere in the region of 5500–6200 K (Alfè et al., 2002a). An independent measure of the likely temperature in the inner core was made by Steinle-Neumann et al. (2001), who performed first-principles calculations of the structure and elasticity of iron at high temperatures; they found that the temperature for which the elastic moduli best matched those of the inner core (including light element depression) was ~ 5700 K.

2.06.6 Physical Properties of Liquid Iron

2.06.6.1 Thermoelastic Properties

The outer core of Earth is liquid Fe–Ni alloyed with 5–10% light elements. Experiments on liquid iron at core conditions are prohibitively challenging. However, once more, from the ab initio simulation of the free energy of pure iron liquid, we can obtain first order estimates for a range of thermodynamic properties at the conditions of Earth's outer core. Figure 27(a)–27(d) shows the results of ab initio calculations for values of density, adiabatic and isothermal bulk moduli,

thermal expansion coefficient, and heat capacity (C_v), respectively, for liquid iron over a range of pressures and temperatures (see Vočadlo et al., 2003b). Results from the experimental analysis of Anderson and Ahrens (1994) for density and adiabatic incompressibility are also shown (as gray lines; upper: 5000 K, lower: 8000 K). The calculations reproduce the experimentally derived density and incompressibility values to within a few percent. It is worth noting that the bulk sound velocity is almost independent of temperature, confirming the conclusion of Anderson and Ahrens (1994).

2.06.6.2 Viscosity and Diffusion

Viscosity is a very important parameter in geophysics because the viscosities of materials in Earth's core are a contributory factor in determining the overall properties of the core itself, such as convection and heat transfer; indeed, the fundamental equations governing the dynamics of the outer core and the generation and sustention of the magnetic field are dependent, in part, on the viscosity of the outer-core fluid. Quantifying viscosity at core conditions is far from straightforward, especially as the exact composition of the outer core is not known. Furthermore, although there have been many estimates made for outer-core viscosity from geodetic, seismological, geomagnetic, experimental and theoretical studies, the values so obtained span 14 orders of magnitude (see Secco, 1995).

Geodetic observations (e.g., free oscillations, the Chandler wobble, length of day variations, tidal measurements, and gravimetry) lead to viscosity estimates ranging from 10 mPas (observations of the Chandler wobble; Verhoogen, 1974) to 10^{13} mPas (analysis of free oscillation data; Sato and Espinosa, 1967). Theoretical geodetic studies (e.g., viscous coupling of the core and mantle, theory of rotating fluids, inner core oscillations, and core nutation) lead to viscosity estimates ranging from 10 mPas (evaluation of decay time of

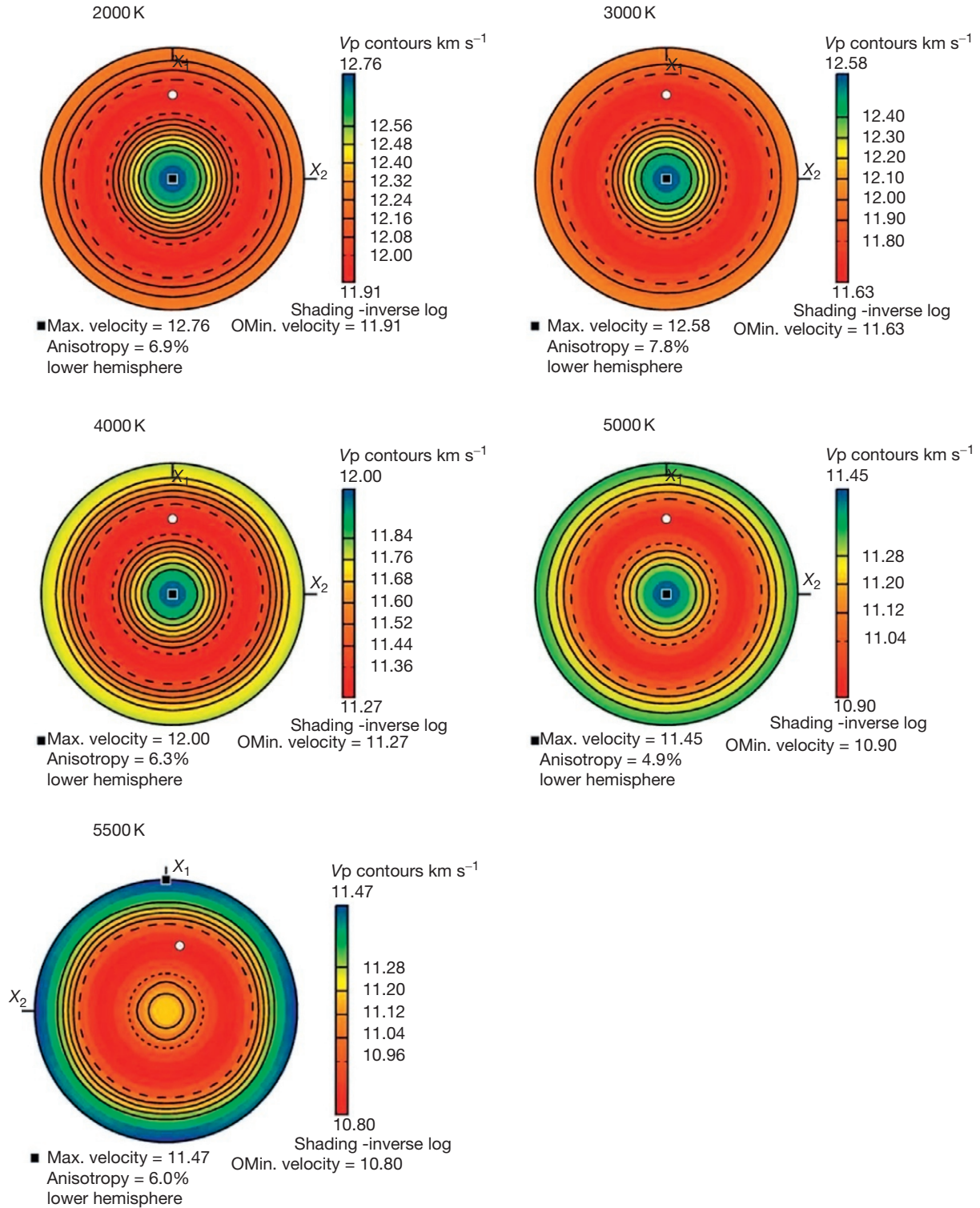


Figure 23 Single-crystal P-wave velocities as a function of propagation direction for hcp-Fe at 316 GPa and temperatures of 2000, 3000, 4000, 5000, and 5500 K. The results at 5500 K are taken from the earlier work (Vočadlo, 2007). Note that the velocities in the $[hk0]$ directions, perpendicular to the c -axis, are gradually becoming more equal to that along the c -axis until above 5000 K, the direction of maximum V_p changes from $[001]$ to $[hk0]$. Reproduced from Vočadlo L, Dobson D, and Wood IG (2009) Ab initio calculations of the elasticity of hcp-Fe as a function of temperature at inner-core pressure. *Earth and Planetary Science Letters* 288: 534–538.

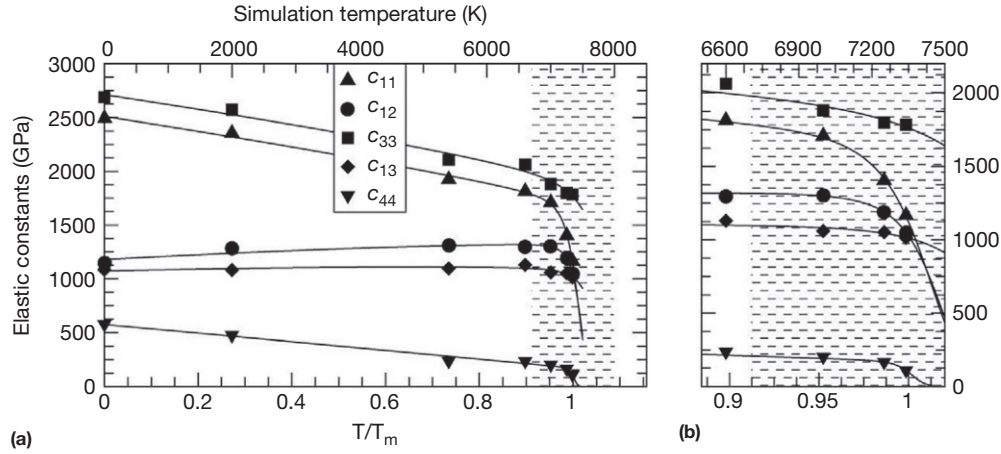


Figure 24 Calculated elastic constants for hcp-Fe as a function of temperature at 360 GPa. The gray band represents the minimum and maximum melting temperatures in the literature for hcp-Fe at 360 GPa. (a) The complete temperature range. (b) Results in the nonlinear regime. Reproduced from Martorell B, Brodholt J, Wood IG, and Vočadlo L (2013b) Strong pre melting effect in the elastic properties of hcp-Fe under inner core conditions. *Science* 342: 466.

inner core oscillations; Won and Kuo, 1973) to 10^{14} mPas (secular deceleration of the core by viscous coupling; Bondi and Lyttleton, 1948). Generally, much higher values for viscosity (10^{10} – 10^{14} mPas) are obtained from seismological observations of the attenuation of P- and S-waves through the core (e.g., Jeffreys, 1959; Sato and Espinosa, 1967), and from geomagnetic data (e.g., 10^{10} mPas; Officer, 1986).

The viscosities of core-forming materials may also be determined experimentally in the laboratory and theoretically through computer simulation. Empirically, viscosity follows an Arrhenius relation of the form (see Poirier, 2002):

$$\eta \propto \exp\left(\frac{Q_v}{k_B T}\right)$$

where Q_v is the activation energy, T is the temperature, and k_B is the Boltzmann constant. Poirier (1988) analyzed data for a number of liquid metals and found that there is also an empirical relation between Q_v and the melting temperature, consistent with the generalized relationship of Weertman (1970):

$$Q_v \cong 2.6RT_m$$

This very important result implies that the viscosity of liquid metals remains constant (i.e., independent of pressure) along the melting curve and, therefore, equal to that at the melting point at ambient pressure, which is generally of the order of a few millipascal seconds. Furthermore, Poirier went on to state that the viscosity of liquid iron in the outer core would, therefore, be equal to that at ambient pressure (~ 6 mPas; Assael et al., 2006).

On a microscopic level, an approximation for the viscosity of liquid metals is given by the Stokes–Einstein equation, which provides a relationship between diffusion and viscosity of the form

$$D\eta = \frac{k_B T}{2\pi a}$$

where a is an atomic diameter and D is the diffusion coefficient.

Theoretical values for diffusion coefficients have been obtained from ab initio molecular dynamics simulations on

liquid iron at core conditions (de Wijs et al., 1998), leading to a predicted viscosity of ~ 12 – 15 mPas using the Stokes–Einstein relation given earlier. However, although the Stokes–Einstein equation has proved successful in establishing a link between viscosity and diffusion for a number of monatomic liquids, it is not necessarily the case that it should be effective for alloys or at high pressures and temperatures. Alfè et al. (2002a) used the more rigorous Green–Kubo functions to determine viscosities for a range of thermodynamic states relevant to Earth’s core (Table 1). Throughout this range, the results show that liquid iron has a diffusion coefficient and viscosity similar to that under ambient conditions, a result already suggested much earlier by Poirier (1988). Both ab initio calculations and experiments consistently give viscosities of the order of a few millipascal seconds. More recently, Desgranges and Delhommelle (2007) used classical molecular dynamics calculations to obtain estimates for viscosity of the outer core also of the order of 10 mPas. This suggests that viscosity changes little with homologous temperature, and it is now generally accepted that the viscosity of the outer core is likely to be a few millipascal seconds (comparable to that of water on Earth’s surface).

2.06.6.3 The Structure of Liquid Iron

It has long been established that liquid structure is approximately constant along the melting curve (e.g., Ross, 1969) and here, in the case of iron, there appears to be a truly remarkable simplicity in the variation of the liquid properties with thermodynamic state; indeed, not only are viscosities and diffusivities almost invariant (as described earlier), but structural properties also show a similarly consistent behavior. Alfè et al. (2002a) calculated the radial distribution function of liquid iron as a function of temperature at a density of 10700 kg m^{-3} , representative of that in the upper outer core (Figure 28); between 4300 and 8000 K, the effect of varying temperature is clearly not dramatic, and consists only of the expected weakening and broadening of the structure with increasing T .

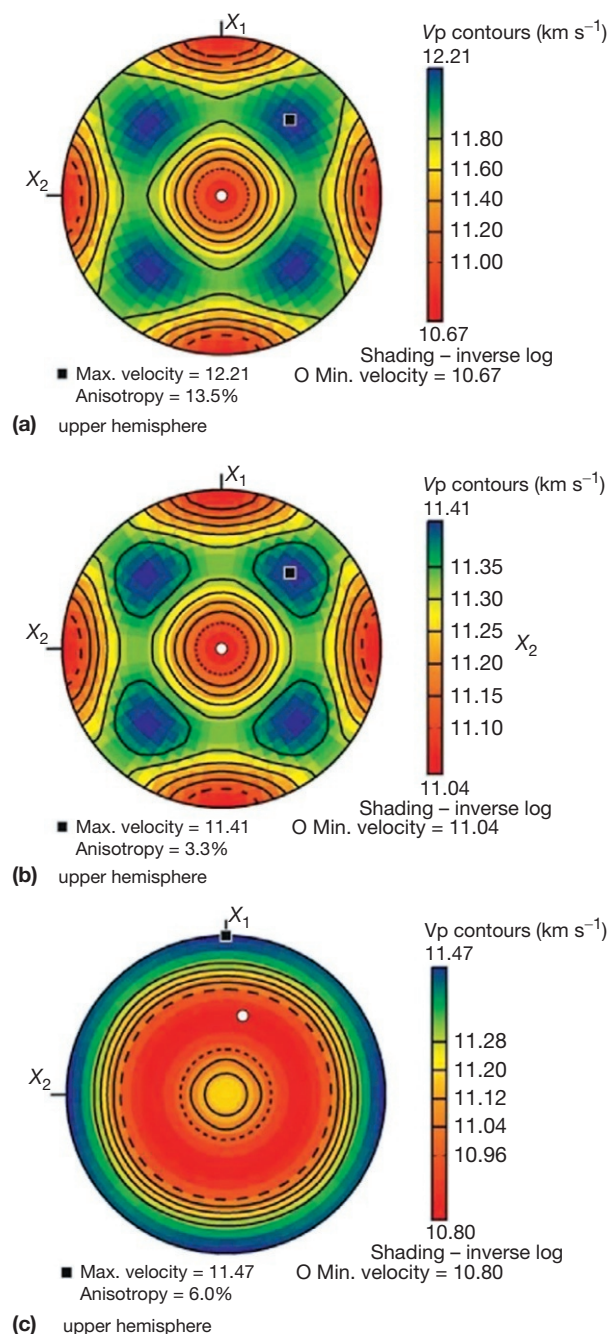


Figure 25 Single-crystal P-wave velocities for (a) fcc-Fe, (b) bcc-Fe and (c) hcp-Fe at inner core conditions as a function of propagation direction.

Furthermore, Shen et al. (2004) determined the structure factors of liquid iron as a function of pressure along the melting curve using x-ray scattering in a laser-heated DAC up to 58 GPa (Figure 29). Once more, the structure factor preserves essentially the same shape, and the behavior is consistent with that of close-packed liquid metals. These results provide structural verification of the theoretical predictions given in Figure 28, and also confirm that it is justifiable to extrapolate viscosities measured under ambient conditions to high pressures.

2.06.6.4 Thermal and Electrical Conductivity of Liquid Iron

The geodynamo is powered by the heat flux in the outer core, which, in turn, depends upon the thermal conductivity of the material present. Estimates for heat flux across the CMB have varied over the years but have generally been estimated to be of the order of 5–15 TW. Recent calculations on iron and iron alloys at the conditions of Earth's core have found that the thermal conductivity is up to three times higher near the top of the outer core than previously thought (de Koker et al., 2012; Pozzo et al., 2012; Figures 30 and 31). The consequences of these results are significant. Such a high conductivity means that heat would accumulate at the top of the core, generating a thick stably stratified thermal layer. As a result, convection in the outer core would be restricted to a small region beneath this layer, suppressing the magnitude and variability of the magnetic field with time. The very high thermal conductivity predicted in the inner core ($<200 \text{ W m}^{-1} \text{ K}^{-1}$) would preclude convection in the inner core. Therefore, anisotropy models based on crystalline alignment as a result of solid-state convection would be incorrect.

2.06.7 Evolution of the Core

Earth's paleomagnetic record suggests that the magnetic field has been operating for over 3 billion years; the fact that this magnetic field exists even today and has not decayed through ohmic dissipation (possible on a timescale of $\sim 10^4$ years) suggests that it is being regenerated and sustained by a process such as a geodynamo. For the geodynamo to work, it requires convection of the core fluid (thermal and/or compositional); whether the core is stable to convection depends on the rate of cooling of the core and, thus, on the evolution of Earth. As the core cools and solidifies, it releases energy via latent heat, much of which is transported across the core via conduction. The thermal conductivity of the core material limits the amount of heat that can be transported in this way, and any excess energy may be used to power the geodynamo. The conductivity (both thermal and electrical) of the core material is, therefore, crucial: if the core material has too high a conductivity, there is no excess heat and, therefore, no dynamo. A further consideration is the heat flow into the base of the mantle. If this is too large, the core would cool too quickly, and the inner core would grow too rapidly; if the heat flow into the mantle is too low, the core would cool too slowly (possibly not crystallizing at all), convection would be hard to initiate and sustain, and magnetic field generation would be difficult.

As a result of the inner core growth, the relative contributions of thermal convection to compositional convection have changed over geological time. Thermal convection would have been dominant in the early stages of Earth's evolution, and would have been the sole power source before the formation of the inner core (possibly ~ 2 billion years ago). However, as the inner core grew, compositionally driven convection (from the preferential partitioning of light elements into the outer core and their subsequent buoyancy) became more important (now responsible for $\sim 80\%$ power to the geodynamo). Two other important factors that affect the thermal evolution of the core are the possible contribution to the heat budget from radioactive decay of, for example, ^{40}K , and the ability of the mantle to

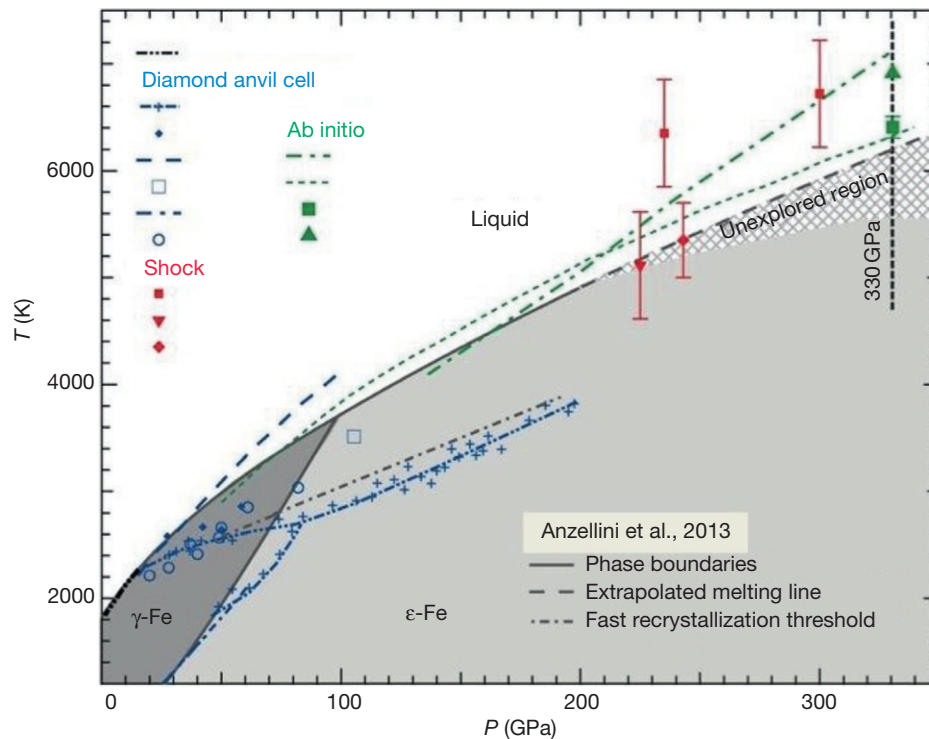


Figure 26 The phase diagram of iron as determined by experiment and theoretical calculations. Diamond anvil experiments (blue): double-dot-dash, Boehler (1993); blue diamonds, Shen et al. (2004); long dash, Williams et al. (1987); open square, Ma et al. (2004); short dash, Komabayashi et al. (2009); open circles, Jackson et al. (2013). Shock data (red): squares, Yoo et al. (1993); diamond, Nguyen and Holmes (2004); triangle, Brown and McQueen (1986). Ab initio calculations (green): dot-dash, Belonoshko et al. (2000); dash, Alfè et al. (2002b); square, Alfè (2009); triangle, Sola and Alfè (2009). Black dot-dash, Swartzendruber (1982). Reproduced from Anzellini S, Dewaele A, Mezouar M, Loubeyere P, and Morard G (2013) Melting of iron at Earth's inner core boundary based on fast X-ray diffraction. *Science* 340: 464–466.

remove heat away from the core. A reliable thermal evolution model has to reproduce: (i) the correct present-day inner core size, (ii) the present-day heat flux (~ 42 TW), (iii) the heat flux through the CMB (estimates range from 2 to 10 TW), (iv) enough entropy to drive a dynamo, and (v) reasonable mantle temperatures.

A number of studies have developed both analytical and numerical models for the thermal evolution of the core on the basis of calculations of heat flux across the CMB coupled with heat balance relations associated with core convection and inner core growth (e.g., Buffett, 2002; Buffett et al., 1992, 1996; Gubbins et al., 2003, 2004; Labrosse, 2003; Labrosse et al., 2001; Nakagawa and Tackley, 2004; Nimmo et al., 2004; Olson et al., 2013; reviewed in Hirose et al., 2013). The requirement for a radiogenic heat source in order to maintain sufficient power to the geodynamo remains a controversial subject. While some models require a radiogenic heat source, such as potassium, to power the geodynamo (Costin and Butler, 2006; Labrosse, 2003; Nimmo et al., 2004), others suggest that convective processes alone are sufficient to maintain the geodynamo (e.g., Buffett et al., 1996; Christensen and Tilgner, 2004).

However, key to all these thermal evolution models is the need for reliable data for material properties at inner core conditions. The results of Pozzo et al. (2012), already mentioned in Section 2.06.6.4, suggest that such a large electrical conductivity would increase heat flow via conduction and, therefore, weaken thermal convection. This implies that a

lower flow velocity is required in the outer core for the same magnetic field, leading to a more stable, possibly stratified, outer core. However, such stratification would suppress magnetic field variations and change the pattern of magnetic field evolution over time.

While mineral physics has made considerable progress (e.g., direct determination of the phase diagram of iron, the quantification of the viscosity of the outer core, the conductivity of iron at core conditions, and the thermodynamic properties of pure iron), key properties in the heat transfer relations, such as the electrical and thermal conductivity, are still not well constrained and need to be validated by experimental data.

2.06.8 The Composition of the Core

2.06.8.1 Bulk Composition

The core is not made from just pure iron; however, the exact composition of Earth's inner core is not very well known. On the basis of cosmochemical and geochemical arguments, it has been suggested that the core is an iron alloy with possibly as much as ~ 10 wt% Ni and very small amounts (only fractions of a wt% to trace) of other siderophile elements such as Cr, Mn, P, and Co (McDonough and Sun, 1995). On the basis of materials-density/sound-wave velocity systematics, Birch (1964) further concluded that the core is composed of iron that is alloyed with a small fraction of lighter elements. The

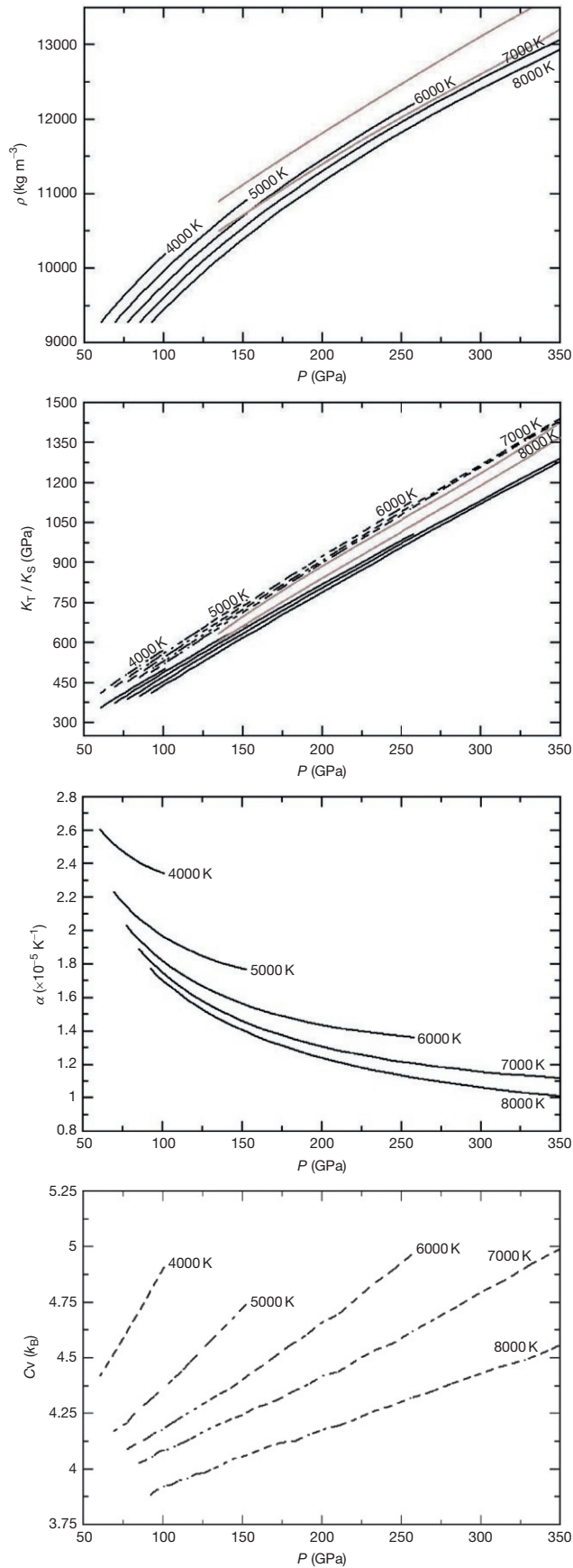


Figure 27 Density, incompressibility, thermal expansion, and heat capacity, as a function of pressure for liquid iron. Black lines: ab initio calculations (Vočadlo et al., 2003b); gray lines: isentropic model determined from experimental data (upper: 5000 K; lower: 8000 K). Reproduced from Anderson WW and Ahrens TJ (1994) An equation of state for liquid iron and implications for the Earth's core. *Journal of Geophysical Research* 99: 4273–4284.

Table 1 The diffusion coefficient D and the viscosity from ab initio simulations of liquid iron at a range of temperatures and densities

		$\rho \text{ (kg m}^{-3}\text{)}$				
		9540	10700	11010	12130	13300
$D \text{ (10}^{-9} \text{ m}^2 \text{ s}^{-1}\text{)}$	3000	4.0 ± 0.4				
	4300		5.2 ± 0.2			
	5000		7.0 ± 0.7			
	6000	14 ± 1.4	10 ± 1	9 ± 0.9	6 ± 0.6	5 ± 0.5
	7000		13 ± 1.3	11 ± 1.1	9 ± 0.9	6 ± 0.6
$\eta \text{ (m Pas)}$	3000	6 ± 3				
	4300		8.5 ± 1			
	5000		6 ± 3			
	6000	2.5 ± 2	5 ± 2	7 ± 3	8 ± 3	15 ± 5
	7000		4.5 ± 2	4 ± 2	8 ± 3	10 ± 3

Source: Alfè D, Kresse G, and Gillan MJ (2000) Structure and dynamics of liquid iron under Earth's core conditions. *Physical Review B* 61: 132–142.

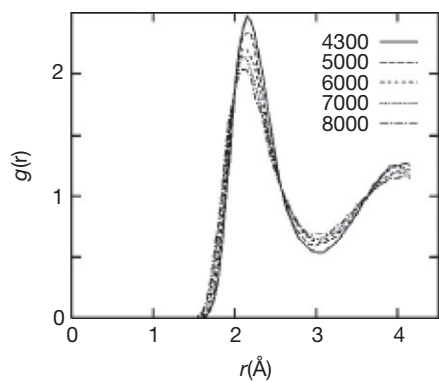


Figure 28 Variation of radial distribution function with temperature from ab initio simulations of liquid iron at the fixed density 10700 kg m⁻³. Reproduced from Alfè D, Kresse G, and Gillan MJ (2000) Structure and dynamics of liquid iron under Earth's core conditions. *Physical Review B* 61: 132–142.

light alloying elements most commonly suggested include S, O, Si, H, and C, although minor amounts of other elements, such as K, could also be present (e.g., Gessmann and Wood, 2002; Poirier, 1994). From seismology, it is known that the density jump across the ICB is between ~4.5% and 6.7% (Masters and Gubbins, 2003; Shearer and Masters, 1990), indicating that there is more light element alloying in the outer core. The evidence thus suggests that the outer core contains ~5–10% light elements, while the inner core has ~2–3% light elements. Our present understanding is that Earth's solid inner core is crystallizing from the outer core as the planet slowly cools and the partitioning of the light elements between the solid and liquid is, therefore, crucial to understanding the evolution and dynamics of the core.

2.06.8.2 The Effect of Nickel

It is generally assumed that the small amount of nickel alloyed to iron in the inner core is unlikely to have any significant effect on the core properties as nickel and iron have sufficiently similar densities to be seismically indistinguishable, and addition of small amounts of nickel is unlikely to appreciably change the physical properties of iron. Experiments at

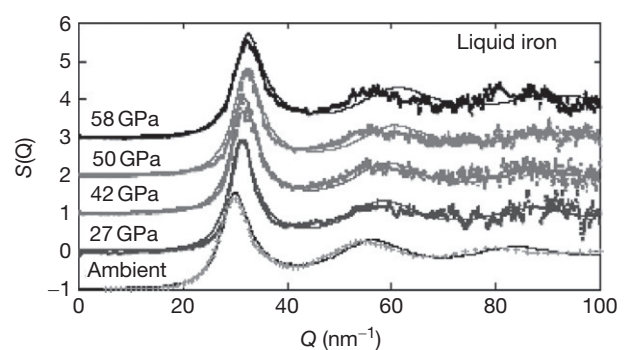


Figure 29 Structure factors of liquid iron along the melting curve determined by x-ray scattering at high pressures. Reproduced from Shen GY, Prakapenka VB, Rivers ML, and Sutton SL (2004) Structure of liquid iron at pressures up to 58 GPa. *Physical Review Letters* 92: #185701.

modestly high pressures and temperatures (72 GPa and 3000 K, Mao et al., 2006; <107 GPa and <2600 K, Komabayashi et al., 2012) show that the presence of nickel stabilizes the fcc phase over the hcp phase, while more recent experiments on Fe_{0.9}Ni_{0.1} at core conditions (340 GPa and 4700 K; Tateno et al., 2012) show the hcp phase to be stable throughout. Kuwayama et al. (2008) used x-ray diffraction experiments to 300 GPa on iron–nickel alloys to propose a number of cooling scenarios for the evolution of the inner core (Figure 32). They suggest that the crystallizing phase depends on the amount of nickel present, and that it was perfectly possible to crystallize the fcc phase and then develop the hcp phase on cooling.

Ab initio calculations at zero Kelvin show that Ni may have an effect on the properties of iron (Vočadlo et al., 2006). The addition of small amounts of nickel (a few atm%) by atomic substitution stabilizes the hcp structure with respect to the bcc structure by up to ~20 GPa. In a more recent study at simultaneous core pressures and temperatures, Côté et al. (2012) showed that the presence of nickel stabilized the fcc phase. Recent ab initio molecular dynamics simulations on Fe–Ni mixtures have produced some very interesting results (Martorell et al., 2013a). The elastic properties of both the hcp and fcc alloy at 360 GPa were calculated at 0 and 5500 K,

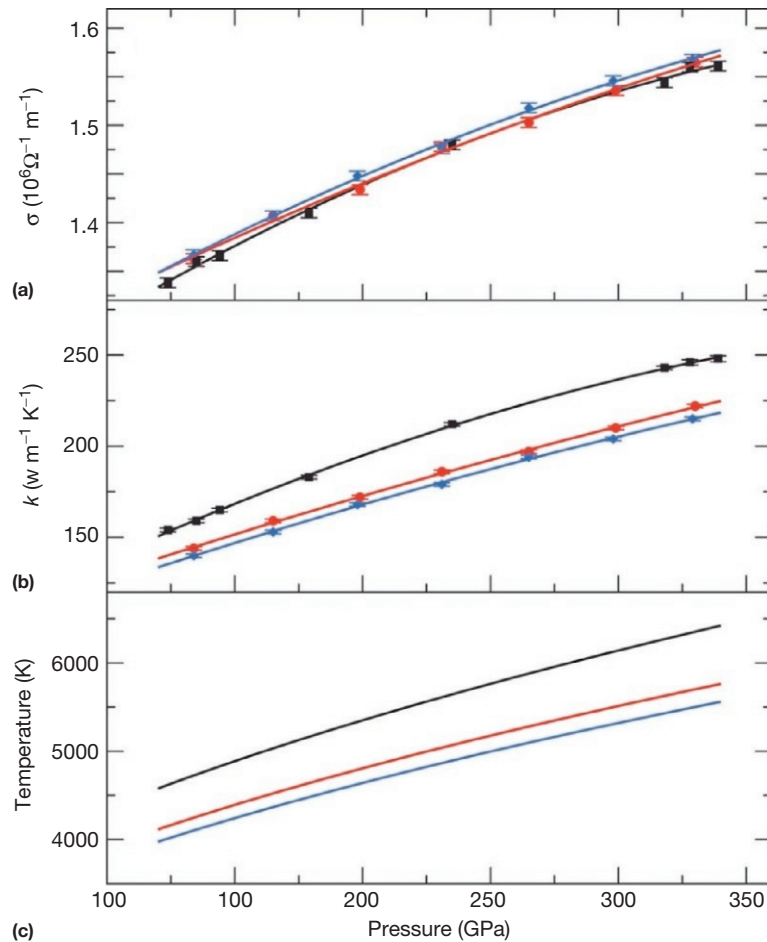


Figure 30 Electrical conductivity, σ (a), and electronic component of thermal conductivity, k (b), of pure iron corresponding to the three outer-core adiabatic profiles (adiabats) displayed in (c). Black lines, adiabat corresponding to the melting temperature of pure iron at ICB pressure; red lines, that of the mixture containing 10% Si and 8% O; and blue lines, that of the mixture with 8% Si and 13% O. Lines are quadratic fits to the first-principles raw data (symbols). Error bars (2 s.d.) are estimated from the scattering of the data obtained from 40 statistical independent configurations. Results are obtained with cells including 157 atoms and the single k-point (1/4,1/4,1/4), which are sufficient to obtain convergence within $<1\%$. Reproduced from Pozzo M, Davies C, Gubbins D, and Alfè D (2012) Thermal and electrical conductivity of iron at Earth's core conditions. *Nature* 485: 355.

and also at 2000 K for the hcp structure. At 0 K, compressional and shear-wave velocities are structure dependent; in the case of fcc, the velocities are very similar to those of pure Fe, but for the hcp structure, the addition of Ni strongly reduces V_s (Figure 33). However, at 5500 K and 360 GPa, Ni has little effect on the wave velocities of the hcp structure, which remain similar to those of pure iron and, in the case of V_s , $>30\%$ greater than that from seismological models. The effect of temperature on Fe–Ni alloys is, therefore, very significant, confirmed by the additional simulations at 2000 K, which reveal a remarkably linear temperature dependence of the change in V_s relative to that of pure iron (Figure 34). The maximum anisotropy in V_p is found to be only very weakly dependent on nickel content, but significantly more dependent on structure (Figure 35). Martorell et al. (2013a) concluded that Ni can safely be ignored when considering its effect on the seismic properties of hcp-Fe under core pressures and temperatures and that the negligible effect of nickel on the physical properties of iron in the core arises not because of

the chemical similarities between iron and nickel, but because of the high temperature of the system.

2.06.8.3 Light Elements

In contrast to the case of nickel, it has long been known that the presence of light elements in the core does have an effect on the core properties. Cosmochemical abundances of the elements, combined with models of Earth's history, limit the possible impurities to a few candidates. The light element impurities most often suggested are sulfur, oxygen, and silicon. But none of these light elements satisfy all the requirements imposed by seismology, geochemistry, and evolutionary models. Given that the liquid outer core is surrounded by a silicate lower mantle, it is not surprising that silicon and/or oxygen are prime candidates for the light elements in the outer core, and the few percent silicon hidden in the core conveniently accounts for the 'missing' silicon in the mantle. Further support for silicon and/or oxygen comes from arguments

based on volatility data, which tend to reject the more volatile carbon and sulfur (among others) in favor of silicon. In the case of oxygen, however, there has been a problem, because geochemical models of Earth's early evolution suggested that the core could have formed only with little or no oxygen (Huang et al., 2011; Wood et al., 2006). However, a recent study (Siebert et al., 2013) indicates that, conversely, the core could actually have formed under oxidizing conditions, thereby making oxygen a viable candidate for a light element in the core after all.

These alloying systems (and others) have been extensively studied experimentally up to pressures of around 270 GPa

(e.g., Antonangeli et al., 2010; Fiquet et al., 2009; Li and Agee, 2001; Lin et al., 2003; Rubie et al., 2004; Sata et al., 2010) and simultaneously high pressures and temperatures up to about 240 GPa and 4000 K (e.g., Fischer et al., 2012; Kamada et al., 2010; Lord et al., 2009, 2010; Mao et al., 2012; Morard et al., 2011; Ozawa et al., 2010), with the experimental pressure and temperature limits being pushed higher all the time. Light elements have also been the focus of several theoretical studies (e.g., Côté et al., 2008a,b, 2010; Martorell et al., 2013a; Pozzo et al., 2013; Tsuchiya and Fujibuchi, 2009; Vočadlo, 2007; Vočadlo et al., 2002; Weerasinghe et al., 2011; Zhang and Oganov, 2010).

2.06.8.3.1 The effect of light elements on the stable phase of iron in the inner core

Both experimental and computational studies of the effects of S, Si, O, and C on the high-P/T phase diagram of iron have shown that the inclusion of light elements in solid iron generally enhances the stability of the bcc structure (Côté et al., 2008a,b; Lin et al., 2002; Sata et al., 2008; Vočadlo et al., 1999). This might be expected as the high-pressure polymorphs of several binary alloys of iron take the CsCl structure, which is topologically equivalent to bcc. Vočadlo et al. (1999) predicted a transition to the CsCl structure of FeSi at ~13 GPa, which was subsequently found experimentally (Dobson et al., 2002); other calculations put the transition somewhat higher (20 GPa, Zhang and Oganov, 2010; 40 GPa, Caracas and Wentzcovitch, 2004), but certainly by core pressures there is little doubt that CsCl–FeSi is the most stable. Sata et al. (2008) found a new CsCl phase of FeS above 180 GPa using synchrotron x-ray diffraction techniques. Lin et al. (2002) used laser-heated DAC experiments to show that the presence of 7.9 wt% silicon stabilized the bcc phase of iron by up to 40 GPa (Figure 36); this was subsequently confirmed by ab initio simulations at zero Kelvin (Côté et al., 2008a). Similar calculations at zero Kelvin (Côté et al., 2008b) also showed that small amounts (6.25 and 12.5 atm%) of C, S, and O also stabilized the bcc structure over the hcp phase. Furthermore, even more recent lattice dynamics calculations (Côté et al., 2010) show that at the pressures and temperatures of Earth's inner core, 7 wt% silicon stabilizes the fcc phase over the hcp

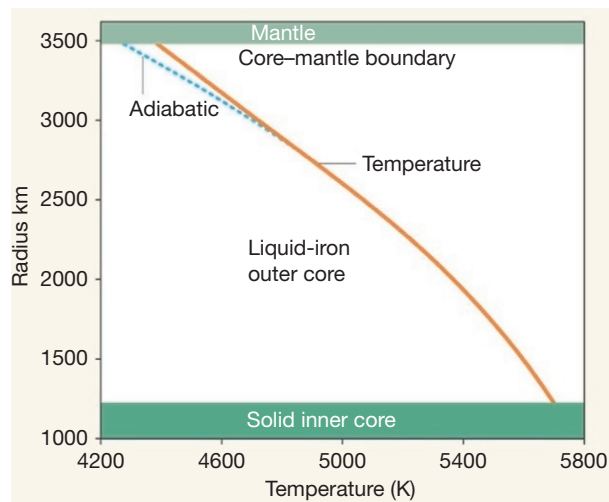


Figure 31 The liquid-iron outer core lies between the mantle and the solid inner core. The increase in temperature across the liquid outer core is well described by an adiabatic process, in which no heat transfer occurs between ascending and descending liquid-iron parcels. Thermal conduction carries heat toward the top of the core. Pozzo and colleagues' study (Pozzo et al., 2012) indicates that heat conduction inside the core may exceed the flow of heat across the core–mantle boundary. As a result, the temperature in the boundary region departs from the adiabatic profile to match the boundary's heat flow. Reproduced from Buffett BA (2012) Geomagnetism under scrutiny. *Nature* 485: 319–320.

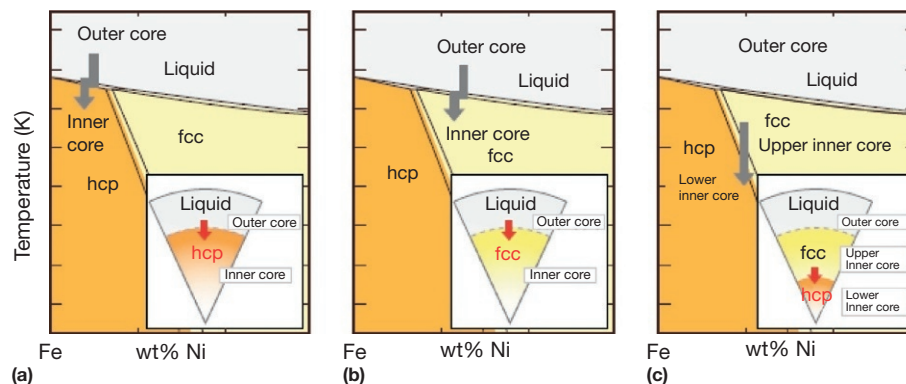


Figure 32 Schematic phase diagrams of the iron–nickel system at the pressure of the inner core boundary. (a) If the Ni content in the outer core is less than that of the fcc–hcp–liquid triple point, the inner core could be composed of the hcp phase; (b) if the nickel abundance in the outer core is larger than that of the triple point, the fcc phase should be first crystallized at the inner core boundary; (c) the fcc phase may transform to an hcp structure at the deep inner core with secular cooling. Reproduced from Kuwayama Y, Hirose K, Sata N, and Ohishi Y (2008) Phase relations of iron and iron–nickel alloys up to 300 GPa: Implications for composition and structure of the Earth's inner core. *Earth and Planetary Science Letters* 273: 379.

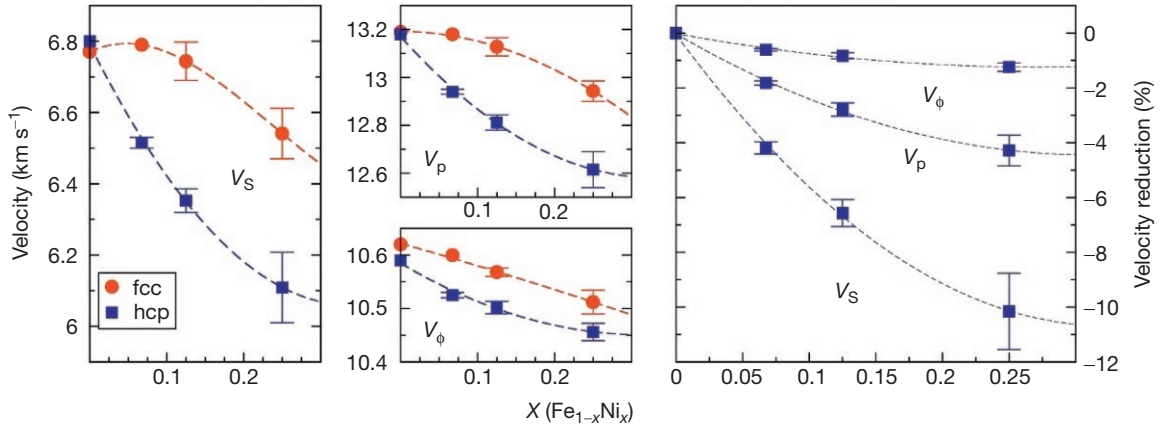


Figure 33 Calculated seismic velocities V_S , V_P , and V_ϕ at 360 GPa and 0 K for fcc (circles), and hcp (squares) structures. For the hcp structure, the relative variations (%) of wave velocities with respect to pure Fe are also shown. Error bars represent the range of values obtained for several configurations at each composition. The dashed lines are guides to the eye obtained by fitting second-order polynomials. Reproduced from Martorell B, Brodholt J, Wood IG, and Vočadlo L (2013) The effect of nickel on the properties of iron at the conditions of the Earth's inner core: Ab initio calculations of seismic wave velocities of Fe–Ni alloys. *Earth and Planetary Science Letters* 365: 143–151.

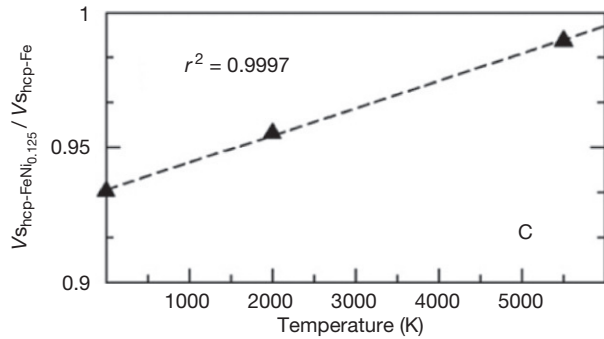


Figure 34 Ab initio calculations of the ratio of V_S between hcp- $\text{Fe}_{0.875}\text{Ni}_{0.125}$ and that of pure hcp-Fe as a function of temperature together with a linear trendline. Reproduced from Martorell B, Brodholt J, Wood IG, and Vočadlo L (2013a) The effect of nickel on the properties of iron at the conditions of the Earth's inner core: Ab initio calculations of seismic wave velocities of Fe–Ni alloys. *Earth and Planetary Science Letters* 365: 143–151.

phase, although more recent experiments at pressures and temperatures of up to ~ 260 GPa and 3600 K show that the alloy remains in the hcp phase (Asanuma et al., 2008; Lin et al., 2009). Experiments on an Fe–16 wt% Si alloy find the high-pressure/high-temperature region of the phase diagram to be a mixture of both hcp- and bcc-type phases (Fischer et al., 2012). Structure-search calculations on iron silicides (Zhang and Oganov, 2010) find that only the CsCl phase of FeSi is thermodynamically stable at core pressures, all other silicides decomposing into Fe + FeSi. This further supports the suggestion that there may be regional bcc stability in Earth's inner core. Experiments on powdered Fe mixed with FeS found the high-pressure/high-temperature region of the phase diagram to contain Fe with Fe₃S in coexistence (Kamada et al., 2010).

2.06.8.3.2 Chemical potential calculations of Fe–X binary systems

An alternative approach to understanding the composition of the inner core is to simulate the partitioning of Fe–X alloys

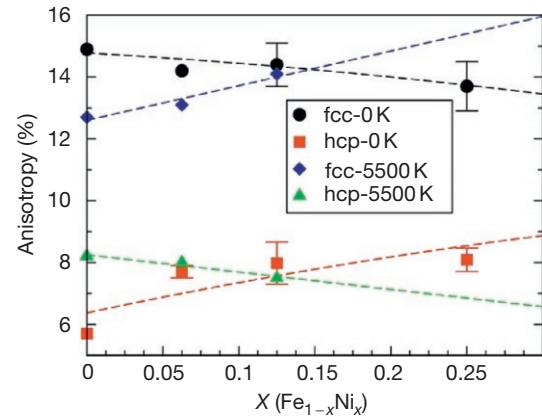


Figure 35 Calculated maximum anisotropy at 0 K for V_P for fcc (circles), and hcp (squares) structures at 360 GPa. Anisotropy for high-temperature hcp structures at 2000 and 5500 K is also displayed (diamonds and triangles, respectively). Error bars represent the range of values obtained for several configurations at each composition. The dashed lines are guides to the eye obtained by fitting second-order polynomials (linear fits for 5500 K; no line is shown for the 2000 K values). Reproduced from Martorell B, Brodholt J, Wood IG, and Vočadlo L (2013) The effect of nickel on the properties of iron at the conditions of the Earth's inner core: Ab initio calculations of seismic wave velocities of Fe–Ni alloys. *Earth and Planetary Science Letters* 365: 143–151.

between the inner and outer cores. Alfé et al. (2000b, 2002a,b) calculated the chemical potentials of iron in binary systems alloyed with sulfur, oxygen, and silicon. They developed a strategy for constraining both the impurity fractions and the temperature at the ICB based on the supposition that the solid inner core and liquid outer core are in thermodynamic equilibrium at the ICB. For thermodynamic equilibrium, the chemical potentials of each species must be equal on both sides of the ICB, which fixes the ratio of the concentrations of the elements in the liquid and in the solid, which, in turn, fixes the densities. The mole fractions required to reproduce the liquid core density are 16%, 14%, and 18%, respectively, for

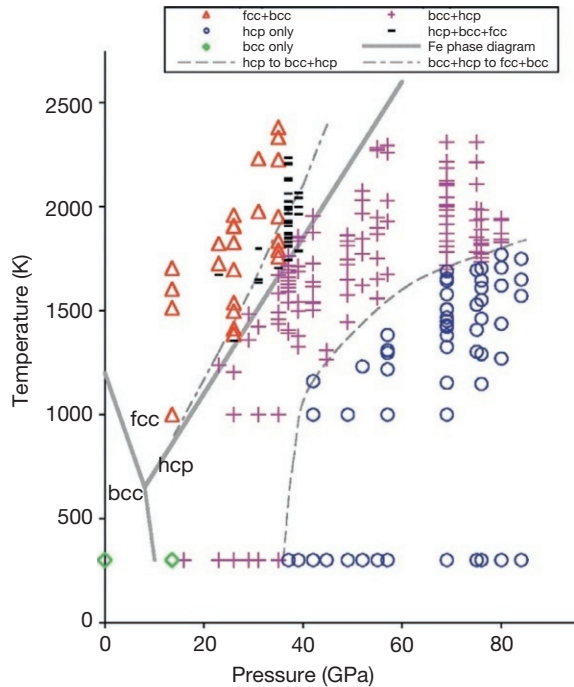


Figure 36 Iron-silicon phases observed in laser-heated diamond anvil cell experiments with the starting materials of Fe (7.9 wt% Si). The presence of silicon stabilizes the bcc phase with respect to the hcp phase by up to ~40 GPa at high temperatures. Reproduced from Lin JF, Heinz DL, Campbell AJ, Devine JM, and Shen GY (2002). Iron-silicon alloy in the Earth's core? *Science* 295: 313–315.

S, Si, and O (Figure 37(a)). If the core consisted of pure iron, equality of the chemical potential (the Gibbs free energy in this case) would tell us only that the temperature at the ICB is equal to the melting temperature of iron at the ICB pressure of 330 GPa. With impurities present, the ab initio results reveal a major qualitative difference between oxygen and the other two impurities: oxygen partitions strongly into the liquid, but sulfur and silicon partition equally in the solid and liquid. This is shown in Figure 37(b): the calculated chemical potentials in the binary liquid and solid alloys give mole fractions in the solid that would be in equilibrium with these liquids – at liquid impurity concentrations corresponding to the seismically observed density in Figure 37(a) – of 14%, 14%, and 0.2% for S, Si, and O, respectively. Having established the partitioning coefficients, Alfè et al. (2000b, 2002a,b) then investigated whether the known densities of the outer and inner cores, estimated from seismology, could be matched by one of their calculated binary systems. For sulfur and silicon, their ICB density discontinuities were considerably smaller than the known seismological value at the time of $4.5 \pm 0.5\%$ (Shearer and Masters, 1990); for oxygen, the discontinuity was markedly greater than that from seismology. The partial volumes in the binary solids give ICB density discontinuities of $2.7 \pm 0.5\%$, $1.8 \pm 0.5\%$, and $7.8 \pm 0.2\%$, respectively (Figure 37(c)). They concluded, therefore, that none of these binary systems are plausible, that is, the core cannot be made solely of Fe/S, Fe/Si, or Fe/O. However, the seismic data can clearly be matched by a ternary/quaternary system of iron and oxygen together with sulfur and/or silicon. A system consistent

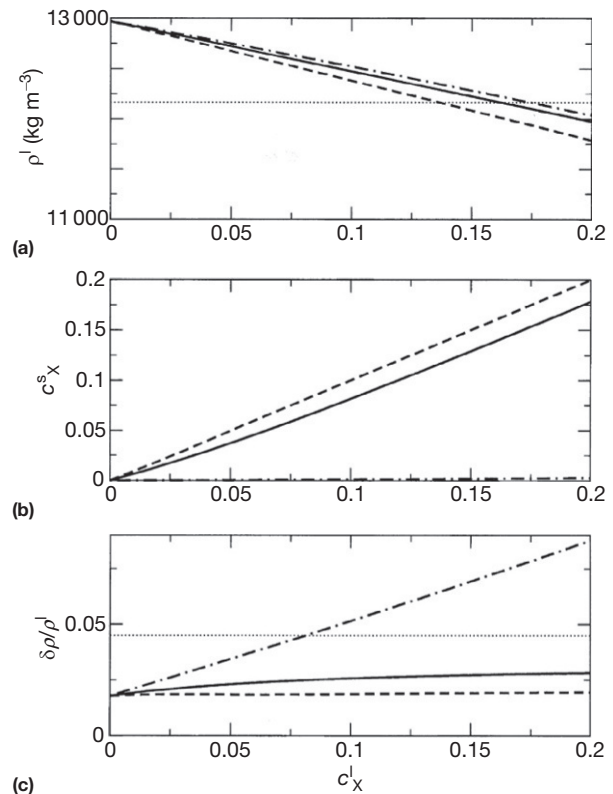


Figure 37 Liquid and solid impurity mole fractions c_x^l and c_x^s of impurities $x = \text{S, Si, and O}$, and the resulting densities of the inner and outer cores predicted by ab initio simulations. Solid, dashed, and chain curves represent S, Si, and O, respectively. (a) Liquid density ρ^l (kg m^{-3}); horizontal dotted line shows density from seismic data. (b) Mole fractions in solid resulting from equality of chemical potentials in solid and liquid. (c) Relative density discontinuity ($\delta\rho/\rho^l$) at the ICB; horizontal dotted line is the value from free oscillation data. Reproduced taken from Alfè D, Gillan MJ, Vočadlo L, Brodholt JP, and Price GD (2002) The ab initio simulation of the Earth's core. *Philosophical Transactions of the Royal Society A* 360: 1227–1244.

with seismic data could, for example, contain 8 mol% oxygen and 10 mol% sulfur and/or silicon in the outer core, and 0.2 mol% oxygen and 8.5 mol% sulfur and/or silicon in the inner core (Alfè et al., 2002a,b). However, it should be remembered that it is likely that several other light elements could exist in the inner core and would therefore have to be considered before a true description of inner core composition could be claimed.

Having oxygen and silicon together in the core poses a problem. When experimentalists try to put oxygen and silicon into liquid iron, their results indicate that the elements seem to be mutually exclusive – in fact, in the steel industry, silicon has been used as a deoxygenating agent. Furthermore, this incompatibility has been found to persist at the high pressures (40–60 GPa) and temperatures (less than about 3000 K) expected during core formation in the early stages of Earth's evolution. Tsuno et al. (2013) performed experiments at a pressure of 25 GPa and a temperature of about 3000 K on samples consisting of a liquid iron-rich metal interfaced with liquid silicate. The samples also included an iron oxide buffer. They then determined the distribution of silicon and oxygen

between the silicate and the metal alloy, and used the results to develop a thermodynamic model of the system. This model predicts that, when the temperature is increased by only a few hundred degrees (from 3000 to 3500 K), the amounts of silicon and oxygen present in liquid iron increase to well above those required to match the density deficit inferred from seismic-wave data. The experiments were performed at relatively modest temperatures (about 3000 K), and so their conclusion that silicon is more readily incorporated into liquid iron alloyed with oxygen at 3500 K is based on an extrapolation of their data. However, these conclusions are supported by high P–T partitioning experiments (Siebert et al., 2013) and silicate-iron reaction experiments (Takafuji et al., 2005).

2.06.8.3.3 Elasticity of FeSi and FeS

A fundamental step toward resolving the structure and composition of Earth's inner core is to obtain the elastic properties of the candidate phases that could be present. Previous work has already suggested that oxygen (see earlier) and carbon (e.g., Vočadlo et al., 2002) are unlikely to be the light elements in the inner core, while the presence of hydrogen seems questionable as the quantities needed to produce the required density deficit are improbably high (Poirier, 1994), although this certainly cannot be ruled out. Furthermore, experiments (Lin et al., 2002; Figure 26) and theory (Côté et al., 2008a,b) show that the presence of silicon has a significant effect on the phase diagram of iron, significantly stabilizing the bcc phase with respect to the hcp phase.

From experimental and theoretical work, we already know that the shear-wave velocities of pure hcp-Fe at high pressures are significantly higher than those of the inner core as inferred from seismology (Antonangeli et al., 2004; Vočadlo, 2007); indeed, they may be higher by as much as 30% (Martorell et al., 2013b). Now we would like to see if the addition of light elements will enable us to reconcile the seismological and mineralogical models. Figure 38 shows the P-wave velocity of FeSi as a function of density compared to the experiments of Badro et al. (2007). The agreement is excellent, confirming that this phase exhibits Birch's law type behavior (see Section 2.06.4.4).

Figure 39 shows how the bulk sound velocity varies for both FeS and FeSi as a function of density for both athermal and hot ab initio calculations together with values from PREM (Dziewonski and Anderson, 1981). Once again, as for pure iron, there seems to be little dependence on temperature of $V_{\phi}(\rho)$.

However, calculations at zero Kelvin and high pressure on $\text{Fe}_{0.875}\text{Si}_{0.125}$ (Tsuchiya and Fujibuchi, 2009) and at high pressure and high temperature on Fe–Si alloys (Martorell et al., 2013b) show that small amounts of silicon have the opposite effect in the hcp phases, reducing the shear moduli and also the shear-wave velocities significantly at 360 GPa (by 15%). This is of considerable importance as it suggests that a viable mineralogical composition that matches seismological data could well be achievable.

A recent analysis of available V_P – ρ systematics on iron and iron alloys shows a slightly different behavior compared to the linearity evident here (Mao et al., 2012). In their study, they suggest that such velocity–density systematics for iron alloys is better represented by a power-law function with concave

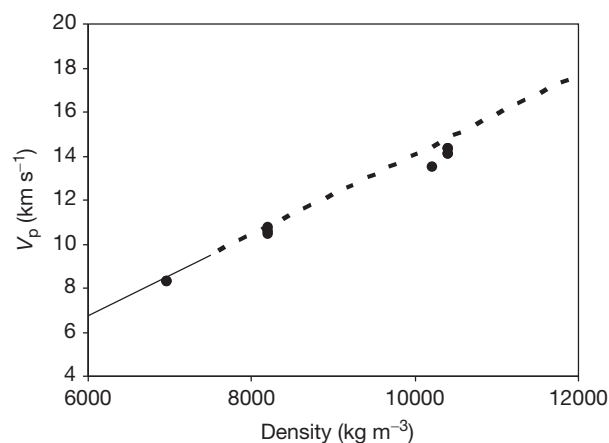


Figure 38 P-wave velocity as a function of density for FeSi compared with the high-P ambient-T DAC experiments of Badro et al. (2007); solid line is the fit to data, dashed line is an extrapolation of the fit. Circles: calculated FeSi- V_P at different temperatures. Reproduced from Vočadlo L (2007) Ab initio calculations of the elasticity of iron and iron alloys at inner core conditions: Evidence for a partially molten inner core. *Earth and Planetary Science Letters* 254: 227–232.

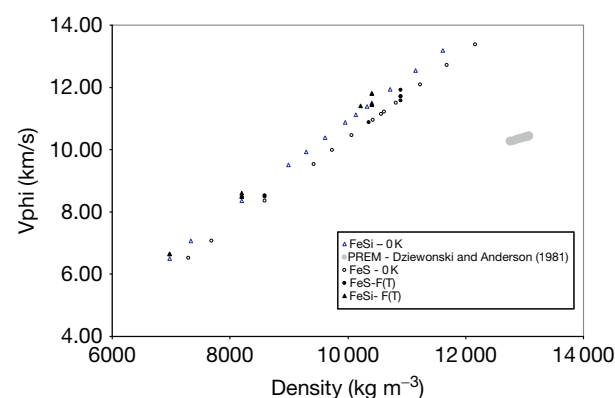


Figure 39 Calculated bulk sound velocity as a function of density for FeS and FeSi (together with those for pure Fe) (Vočadlo, 2007) compared with PREM (Dziewonski and Anderson, 1981).

behavior (Figure 40). It is clear, with such a plethora of data, that a unique solution regarding the composition of Earth's core cannot be achieved by this method, although the authors suggest that iron alloyed with ~8 wt% silicon is the most likely solution for an inner core at 6000 K (Figure 41).

The calculated P-wave anisotropy for both FeS and FeSi is, as might be expected, very similar to that of pure iron, with a value of ~6%. The seismically observed anisotropy (3–5%; Song and Helmberger, 1998) and layering in the inner core could, therefore, be accounted for by either of these phases if the crystals were randomly oriented in the isotropic upper layer and partially aligned in the anisotropic lower layer. However, again, V_S at viable core temperatures (i.e., >5000 K) is much higher than that inferred from seismology (10–30%), in agreement with inferences drawn from the extrapolation of lower pressure experimental data (Antonangeli et al., 2004) and also with the value of 4.04 inferred from shock experiments at a density of 12770 kg m⁻³ (Brown and McQueen, 1986). So,

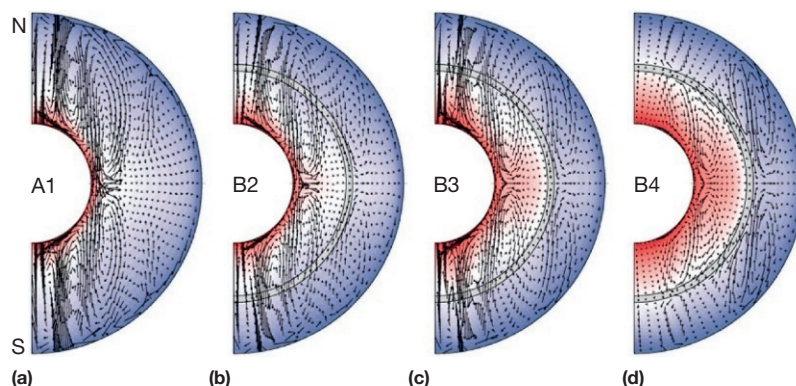


Figure 42 Numerical simulation results on core convection. (a–d) Meridional cross-section of the core flow (arrows) and temperature (red, hot; blue, cold) averaged over longitude and time for different models (A1 and B2–B4). Gray middle layer in (b–d) represents the nominal range of the liquid structural boundary. The change in the Fe–O bonding environment leads to layering, which suppresses convection. Reproduced from Ozawa H, Hirose K, Tateno S, Sata N, and Ohishi Y (2010) Phase transition boundary between B1 and B8 structures of FeO up to 210 GPa. *Physics of the Earth and Planetary Interiors* 179:157–163.

core cooling rate or a higher concentration of radiogenic elements in the core or a combination of the two. Moreover, a faster cooling rate implies that the inner core, which is already thought to be a relatively young feature of Earth, is even younger.

2.06.9 Summary

It is clear that mineral physics has a very important role to play in improving our understanding of the structure, composition, and evolution of Earth's core. With increasing computer power and the advancing sophistication and precision of experimental techniques, reaching ever higher pressures and temperatures, more complex systems will be able to be explored at the conditions of Earth's core. Results from this research will enable many of the questions concerning Earth's core to be resolved. The key issues are as follows:

1. Seismological evidence for anisotropy and layering in the inner core is strong, but the mechanism by which this is occurring is unclear at present. With the presence of light elements, it is distinctly possible that the inner core phase is not just hcp-Fe, but has two or more phases of iron contributing to the anisotropy and layering. Conversely, both these phenomena could be entirely down to growth mechanisms and, therefore, probably only one phase needs to be present. Full quantification of the thermoelastic properties of multicomponent iron alloy systems at the conditions of Earth's inner core would enable a compositional model to be developed that is consistent with the increasingly accurate seismological data.
2. More precise seismological data, particularly shear-wave velocities, along with a better understanding of anelasticity in the inner core, would help us better understand the detailed structure of the inner core.
3. Super rotation of the inner core now seems to be marginal, yet a better understanding of the rheology of the multicomponent systems present would both confirm this and allow an evolutionary model to be developed that is consistent with the present-day Earth.

4. The temperature profile of the core is still unknown; in particular, the melting temperature of iron at the ICB pressures may be higher than previously thought, and it is far from clear exactly what the effect of light elements and/or nickel will be on this quantity.
5. Mineral physics constraints on the thermoelastic properties and processes of multicomponent liquids are essential to both the magnetohydrodynamics relations governing the geodynamo and the core evolution models that determine the age and heat budget of Earth; of particular import are further estimates, both experimental and theoretical, of key parameters for thermal evolution and dynamo models such as electrical and thermal conductivity.
6. Composition models for the outer core can also help clarify the possible structure of the outer core at both the crystallization surface at the ICB and the iron-silicate reaction zone at the CMB.

Mineral physics may soon have many of the answers to these problems, but results from such advanced theoretical and experimental techniques are nothing without well-constrained seismological data. Models of core composition, structure, and evolution can be believed only when the mineral physics data exactly match the primary seismological observations. This multidisciplinary approach is the only way forward for a full and thorough understanding of Earth's core.

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2.07 Mineralogy of Super-Earth Planets

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2.07.1 Introduction

The past two decades in modern astronomy have seen astounding success in discovering planets orbiting stars beyond the solar system. Starting with the first detections of planets orbiting neutron stars (Wolszczan and Frail, 1992) and those orbiting sunlike stars (Marcy and Butler, 1996; Mayor and Queloz, 1995), over 900 confirmed extrasolar planets or ‘exoplanets’ are now known. These planets have been discovered by a variety of techniques. By far, the largest number has been identified by the radial velocity method, which involves observing the wobbling of the host star due to the gravitational pull by the planet along the line of sight of the observer. The amplitude of the radial velocity of the stellar motion places a lower limit on the planetary mass, while the period gives the orbital period of the planet. Another major approach to exoplanet detection has been the transit method,

whereby the passage of the planet in front of the host star is seen in the temporary dimming of the stellar light as observed from Earth. The transit method ushered in a major advance in the characterization of exoplanets as it allows the measurement of the planetary radius and the orbital inclination of the system, which conclusively determines the planetary mass when radial velocity observations are available. One of the greatest successes in discovering exoplanets have been achieved by the Kepler space telescope (Batalha et al., 2013; Borucki et al., 2010), which has discovered (as of July 2013) 134 confirmed exoplanets and over 3200 exoplanet candidates with a wide range of exoplanetary properties. Exoplanets have also been detected by other methods such as pulsar timing (Wolszczan and Frail, 1992), gravitational microlensing (Gaudi et al., 2008), and direct imaging (Kalas et al., 2008), covering different regions of exoplanet parameter space. For further details, see Chapter 10.21.

The numerous exoplanet discoveries via different methods have also led to the estimation of occurrence rates of exoplanets over a wide range of planetary masses and radii, ranging from gas giant planets to sub-Neptune and even terrestrial-size planets in the solar neighborhood (Fressin et al., 2013; Howard et al., 2012). The available statistics indicate a planetary mass (size) function increasing with decreasing planet mass (size), namely, that giant planets are comparatively rare (Howard et al., 2012; Figure 1). It is estimated that 15% of sunlike stars host at least one planet of 3–30 Earth masses (M_E), and an additional 14% of such stars have planets with 1–3 M_E (Howard, 2013). Correlations of the planet occurrences with the metallicities of the host stars have also suggested that formation of giant planets is positively correlated with the metallicities of the stellar hosts (Fischer and Valenti, 2005), whereas low-mass planets are uncorrelated with the stellar metallicity (Buchhave et al., 2012). Besides the statistical correlations, exoplanets detected to date span a wide diversity in orbital parameters (orbital periods, separations, eccentricities, inclinations, etc.), masses, radii, and temperatures, much wider than the phase space spanned by planets in our solar system. In recent years, it has even become possible to observe the atmospheres of a wide range of exoplanets (e.g., Seager and Deming, 2010).

The latest exoplanet surveys are increasingly focusing on discovering low-mass planets around nearby stars, with the ultimate aim of discovering Earth analogs in nearby stellar systems. To date, masses and radii have already been measured for over a dozen super-Earths, defined as those planets with masses between 1 and 10 M_E (see the succeeding text). Understanding the interiors and atmospheres of these super-Earths represents a new frontier in exoplanet science. There are no super-Earth analogs in our solar system. Limited data available at present suggest that super-Earths may span a wide range of

possible compositions from iron-rich super-Mercuries and molten lava planets to water worlds with thick steamy envelopes and planets dominated by carbon. It is not yet known what fraction of super-Earths are scaled-up versions of terrestrial planets and which are scaled-down versions of ice giants such as Neptune or lie somewhere in the continuum between these compositions.

Knowledge of the mineralogy of super-Earth planets is essential to understanding their interior structure, thermal behavior, and long-term evolution. The mineralogy will depend on bulk composition and the pressures and temperatures of the interior. The large sizes of super-Earth planets mean that interior pressures are very high, posing a severe challenge for laboratory experiments attempting to reproduce super-Earth conditions. Quantum mechanical theoretical methods offer an effective alternative means to evaluate interior mineralogy, but such methods require testing and confirmation by experiment. New laboratory techniques for extending the accessible pressure range are undergoing rapid development. Combined with the fast pace of advances in astronomical detection, observation, and modeling of extrasolar planets, it is clear that the study of super-Earth planets, while in its infancy today, will expand rapidly in the coming years. This chapter reviews our current understanding of mineral behavior at extreme pressure (P)–temperature (T) conditions and its possible implications for super-Earth planets. It is expected that future developments will likely require substantial revisions in this understanding, but much progress has been made to date, and a summary of this progress is undertaken here. Other recent review articles discussing possible internal structures and mineralogy of exoplanets can be found elsewhere (Sotin et al., 2010; Valencia, 2013).

2.07.2 Overview of Super-Earths

2.07.2.1 What Is a Super-Earth?

The term ‘super-Earth’ refers canonically to planets with masses between 1 and 10 M_E (Seager et al., 2007; Valencia et al., 2006). The upper limit of 10 M_E , though not well defined, is motivated by the mass limit beyond which a solid protoplanetary core is expected to be able to gravitationally attract and retain H_2 –He gas from the surrounding nebula and thereby grow into a Neptune- or Jupiter-sized planet. The corresponding radii of super-Earths are generally in the range of 1–2.5 Earth radii, though a few members above 2.5 Earth radii are now known. As discussed elsewhere in this chapter, super-Earths can plausibly encompass a wide range of compositions, but here, we will focus our attention primarily on terrestrial-type compositions, although possible planets enriched in carbon and water will also be discussed.

We expect that the super-Earth family will encompass a broad range of physical properties and orbital characteristics and thus have the potential to exhibit a wide variety of climatic regimes ranging from very hot for planets close to their stars to beyond the ice line for planets at a great distance from their hosts. The question of habitability of super-Earths is obviously one of central importance (Seager, 2013). While this topic is not directly addressed here, the interior mineralogy will influence key habitability factors including the nature and

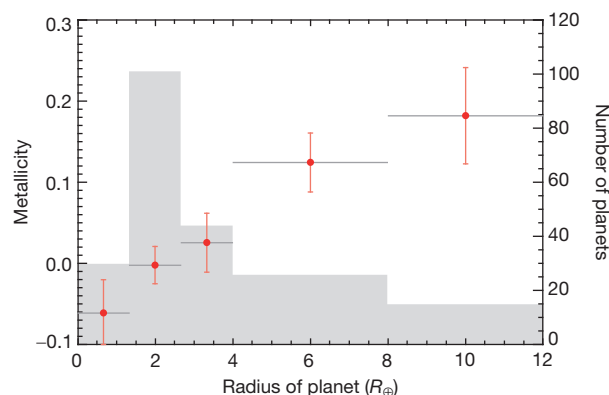


Figure 1 Average metallicity (proportion of elements heavier than H and He) for planet-hosting stars and a number of observed planets plotted as a function of planetary radius. The red symbols show the average metallicity of the host stars with planets of different radii grouped in 1.33 Earth radii and 4 Earth radii bins. The bin size is indicated by the length of the horizontal line, and the uncertainty in the average metallicity is given by the standard deviation. The gray histogram gives the number of planets in each bin. Reproduced from Buchhave et al. (2012) An abundance of small exoplanets around stars with a wide range of metallicities. *Nature* 486: 375–377, with permission.

composition of the atmosphere, existence of plate tectonics, and capacity to generate an internal magnetic field.

With no analogs in the solar system, it is presently unclear what fraction of super-Earths are scaled-up terrestrial planets and what fraction are scaled-down giant planets, which might have lost their primordial envelopes to atmospheric escape. The atmospheres of super-Earths may resemble those of ice giants such as Uranus and Neptune with thick hydrogen-rich atmospheres or terrestrial planets with secondary atmospheres composed of heavy molecules such as CO_2 , O_2 , H_2O , or other components. Other possibilities having no solar system analog include water-dominated atmospheres in planets that formed beyond the snow line and migrated inward or planets with secondary atmospheres of outgassed H_2 (which might affect the radius of the planet even for small amounts of hydrogen) (Rogers and Seager, 2010). Detailed observations and characterization of super-Earths are one of the most dynamic areas of exoplanetary science today, with several unsolved problems at the intersections of astrophysics, planetary science, and geoscience.

2.07.2.2 Observations of Super-Earths

The past few years have seen a rise in the discoveries of super-Earths. Increased photometric precision in transit surveys now allows detection of planets even below Earth's size. However, since transit surveys can only measure the size but not the mass, independent constraints on the planet masses need to be obtained from alternative methods. Using the radial velocity method, currently achievable Doppler precisions have allowed measurement of exoplanet masses down to $\sim 5 M_E$ for super-Earths in close orbits around stars of varied spectral types (Charbonneau et al., 2009; Léger et al., 2009; Winn et al., 2011). An alternative approach to measure mass has been made possible by detections of multiplanet systems by the Kepler space telescope. By measuring the transit timing variations of a transiting exoplanet induced by gravitational interactions with other planets in the system, the mass of the transiting exoplanet can be inferred dynamically. This approach has led to mass measurements of many of the transiting super-Earths known to date. Figure 2 shows the super-Earths for which masses and radii have been measured so far. The Kepler space telescope has discovered all but four of these super-Earths, and the masses of many of them have been determined dynamically. Measuring masses of all these Kepler planets would not have been possible using the radial velocity method alone because their host stars are too faint for the required radial velocity precision. For the same reason, observing the atmospheres of these Kepler planets is very difficult with current observational capabilities.

One of the major thrusts in exoplanet research is to detect super-Earths orbiting low-mass stars and nearby bright stars. The advantage of finding low-mass stars hosting super-Earths is that for a given super-Earth mass and orbital period, the measurement of both the planet mass and the planet radius becomes easier for lower stellar mass and radius – that is, both the radial velocity and the transit signals are larger. On the other hand, brighter stars allow greater precision in the mass and radius measurements. Both these situations are also particularly favorable to observe super-Earth atmospheres, since the favorable

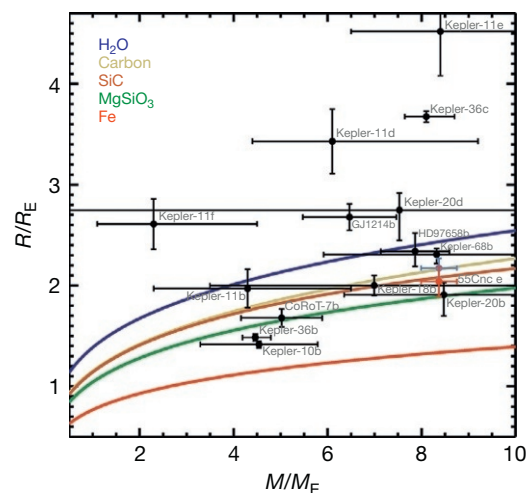


Figure 2 Mass–radius relations of super-Earths. The colored curves show mass–radius relations predicted by internal structure models of solid planets of uniform composition composed of the different species indicated in the legend. The black symbols with error bars show measured radii and masses of known transiting super-Earths. Two possible values of radii are shown for 55 Cancri e (55 Cnc e). The red data point shows the radius measured in the visible, and the blue data point shows a gray radius obtained by combining visible and infrared measurements. For Corot-7b, there are multiple measurements of the mass as discussed in the text. Only the lower mass determination is shown here. Planetary properties were obtained from the Exoplanet Orbit Database (Wright et al., 2011) and the Exoplanet Data Explorer at exoplanets.org. Modified from Madhusudhan N, Lee KKM, and Mousis O (2012) A possible carbon-rich interior in super-Earth 55 Cancri e. *Astrophysical Journal Letters* 759(2): L40. <http://dx.doi.org/10.1088/2041-8205/759/2/L40>, with permission.

stellar parameters allow better precision for spectroscopic observations of the super-Earths in the infrared. Consequently, of all the super-Earths known to date, two are known to be particularly good candidates for detailed characterization of their interiors and atmospheres: (1) GJ 1214b, a super-Earth orbiting a low-mass M Dwarf star, and (2) 55 Cancri e, a super-Earth orbiting a nearby bright sunlike star. These and other super-Earths are discussed in more detail in the succeeding text.

2.07.2.3 Interior Structure and Mass–Radius Relationships

Interior structure models for exoplanets are essential for interpreting observations of their masses, radii, and atmospheres and for understanding the physicochemical diversity of planetary systems. Detailed interior models exist for Earth and other solar system planets satisfying geophysical observables and geochemical and cosmochemical constraints (see Chapter 10.02). Models for exoplanets are constructed in a similar way by assuming a spherically symmetric planet in hydrostatic equilibrium. The planet is taken to be fully differentiated and sorted into layers of increasing density with a fixed composition in each layer. The interior structure is obtained by solving a set of coupled differential equations for mass $m(r)$, pressure $P(r)$, and density $\rho(r)$, using the equations for hydrostatic equilibrium:

$$\frac{dP(r)}{dr} = -\frac{Gm(r)\rho(r)}{r^2} \quad [1]$$

the mass of a spherical shell

$$\frac{dm(r)}{dr} = 4\pi r^2 \rho(r) \quad [2]$$

and an equation of state (EOS)

$$\rho(r) = f(T(r), P(r)) \quad [3]$$

where r is the radial distance from the planet's center, G is the gravitational constant, and T is the temperature.

Depending on composition, the interior models may include layers representing an outer atmosphere or ocean, ice layer, silicate mantle, and metallic core. Some layers may be further subdivided due to phase or chemical changes within a given region. The first detailed interior models for massive terrestrial planets were constructed by Valencia et al. (2006). Subsequently, a number of additional models have been reported (Fortney et al., 2007; Gong and Zhou, 2012; Grasset et al., 2009; Madhusudhan et al., 2012; Rogers and Seager, 2010; Seager et al., 2007; Sotin et al., 2007; Swift et al., 2012; Wagner et al., 2012). In addition to terrestrial-type super-Earths, models have also explored, for example, Fe-rich (super-Mercuries) (Valencia et al., 2006), H₂O-rich ('ocean' planets) (Sotin et al., 2007), and C-rich compositions ('diamond' planets) (Madhusudhan et al., 2012).

The temperature distribution in the interior depends on a number of factors such as the initial temperature resulting from accretion processes, the distribution of heat sources in the interior, and the rate of heat transport, as well as the external boundary condition set by incident irradiation from the host star and any insulating effects of an overlying atmosphere. While the temperature gradient throughout much of the interior is likely to be adiabatic, the actual temperature is only loosely constrained due to the uncertainties mentioned earlier. Some interior models to date have incorporated detailed thermal models by making various assumptions about physico-chemical conditions and thermal properties in the planet, whereas other models have mainly ignored thermal effects or treated them in a simplified manner so far.

Surface temperatures of known super-Earths are expected to range from ~600 to ~2500 K (Figure 3), which is a reflection of the close orbital distances of most detections so far. The upper range of surface temperatures is above the melting temperatures of silicates and thus may result in the formation of a magma ocean and a thick atmosphere due to extensive degassing from the planet's interior. Cooler surface temperatures allow for a brittle crust and potentially volatile-rich oceans and atmospheres.

The interior model constrains mass-radius scaling relationships that allow for interpretation of observational data on exoplanets in terms of composition. For terrestrial compositions, Valencia et al. (2006) obtained the following mass (M)-radius (R) scaling expression for planets with 1–10 M_E :

$$\frac{R}{R_E} = \left(\frac{M}{M_E}\right)^{0.267-0.272} \quad [4]$$

where R_E and M_E are the radius and mass of the Earth. Other studies have reported similar relationships (Grasset et al., 2009; Sotin et al., 2007). For a representative ocean planet containing

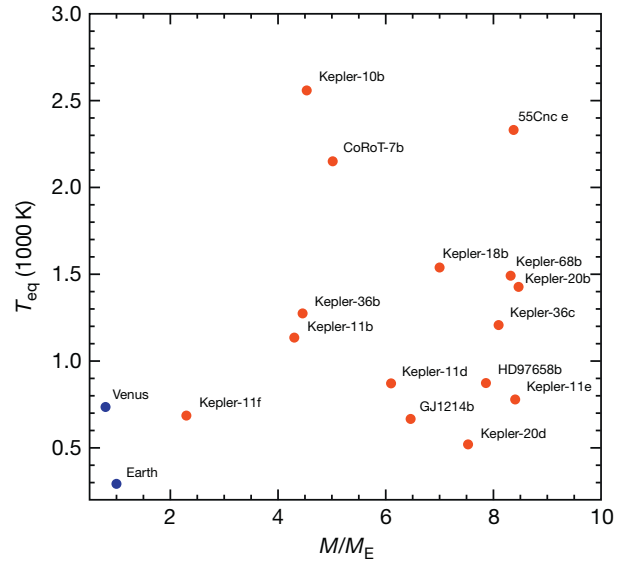


Figure 3 Planetary equilibrium temperature versus mass for super-Earths detected to date. Planetary properties were obtained from the Exoplanet Orbit Database (Wright et al., 2011) and the Exoplanet Data Explorer at exoplanets.org.

50 wt% H₂O and 50 wt% refractory material (rock and metal), the corresponding expression is (Sotin et al., 2007)

$$\frac{R}{R_E} = 1.262 \left(\frac{M}{M_E}\right)^{0.275} \quad [5]$$

The interior models are used to make inferences regarding internal structure and dynamics, cooling histories, magnetic field generation, and other planetary properties. Figure 2 illustrates how the observed mass-radius values for super-Earths compare with predictions from internal structure models for solid planets with selected uniform compositions. These end-member models delineate the ranges of masses and radii that can exist for different categories of planets. In a more detailed approach, Wagner et al. (2012) constructed a four-layer structural model for rocky exoplanets by combining eqns [1]–[3] with energy balance equations and used these to model the structure and internal dynamics of two recently discovered super-Earths. Figure 4 shows the range of interior P - T conditions predicted from their model for selected planetary masses. Other studies produce broadly similar results for terrestrial-type compositions (e.g., Sotin et al., 2007; Valencia et al., 2006). The core-mantle boundary and central pressure as a function of planetary mass are shown in Figure 5, for both the rocky exoplanet modeled by Wagner et al. (2012) and an ocean planet consisting of 50% rocky material of terrestrial composition and 50% H₂O (Sotin et al., 2007). Compared to Earth where the core-mantle boundary pressure is 135 GPa and ~3000–4000 K, the conditions in a 10 M_E terrestrial or ocean planet reach ~1200 GPa and ~6000–7000 K. The corresponding central pressure ranges from ~2400 GPa and ~6500 K (ocean planet) to 3900 GPa and ~10 000 K (terrestrial planet) (compared with 363 GPa and ~6000 K for Earth).

Interpretation of observed mass-radius data for exoplanets in terms of compositional models is limited by observational uncertainties, model assumptions, and inherent degeneracies

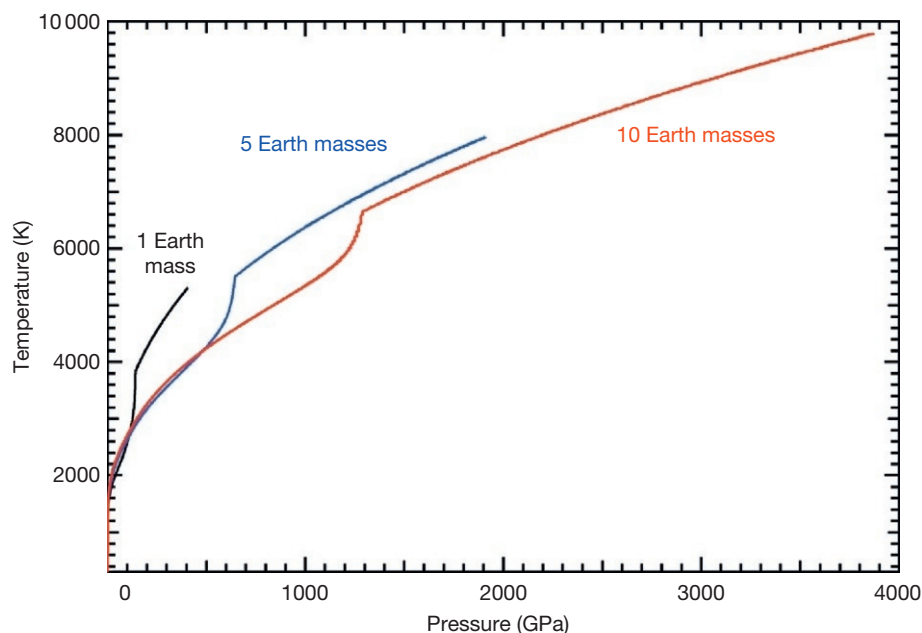


Figure 4 Internal pressures and temperatures from an internal structure model for Earth-like planets for the range of masses indicated. Reproduced from Wagner FW, Tosi N, Sohl F, Rauer H, and Spohn T (2012) Rocky super-Earth interiors. *Astronomy and Astrophysics* 541: A103. <http://dx.doi.org/10.1051/0004-6361/201118441>, with permission.

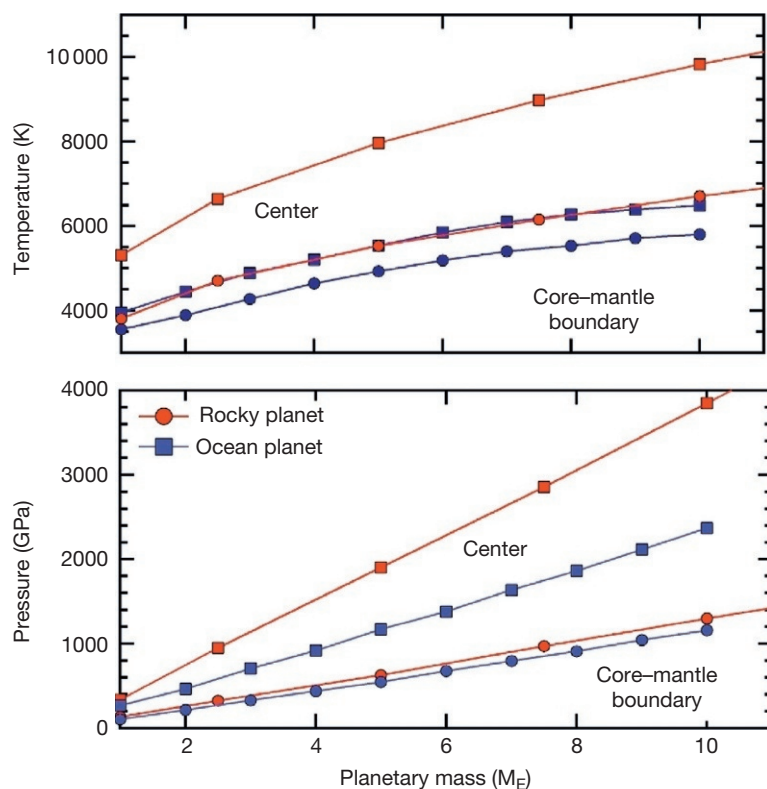


Figure 5 Temperature and pressure at the core–mantle boundary and center of super-Earths as a function of mass for an Earth-like composition (Wagner et al., 2012) and ocean planet containing 50% H₂O (Sotin et al., 2007).

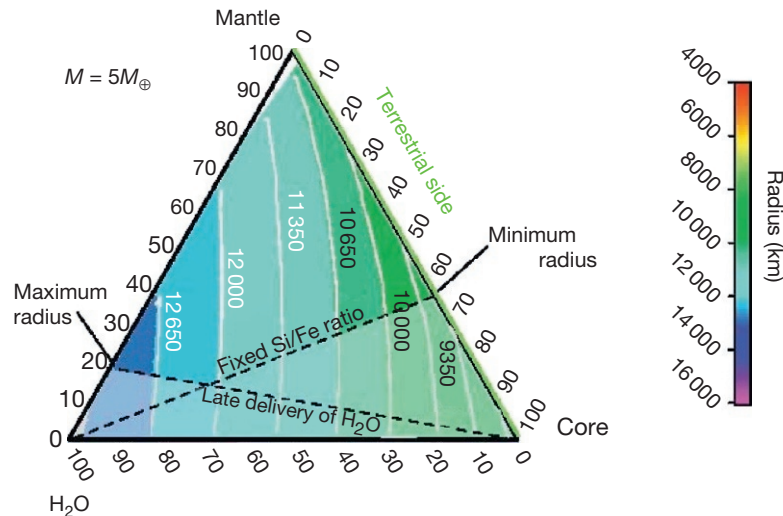


Figure 6 Ternary diagram showing range of possible compositions for a $5 M_{\oplus}$ planet with components of H_2O , mantle (silicate), and core (iron). Each point inside the diagram uniquely specifies a composition and corresponding radius. The smallest radius corresponds to a pure iron planet and the largest radius corresponds to a pure H_2O planet. Reproduced from Valencia D, O'Connell RJ, and Sasselov DD (2009) The role of high-pressure experiments on determining super-Earth properties. *Astrophysics and Space Science* 322(1–4): 135–139. <http://dx.doi.org/10.1007/s10509-009-0034-6>, with permission.

(Rogers and Seager, 2010). There are a variety of sources of observational uncertainties. Planet mass, radius, and equilibrium temperature are measured relative to the host star, so reducing uncertainties in host star properties and improved measurement precision can better constrain planetary properties. Beyond this, there remains a fundamental limitation in the ability to determine composition given the limited constraint of mean density. In many cases, a wide span of compositions can fit the available data (Rogers and Seager, 2010; Valencia et al., 2006). Figure 6 illustrates the compositional degeneracies in a $5 M_{\oplus}$ planet consisting of H_2O , a silicate mantle, and an iron core (Valencia et al., 2009). Additional constraints, such as atmospheric composition, may allow one to distinguish among possible compositions. Uncertainties in model assumptions such as the pressure–temperature–density relation are also important and are discussed further in the succeeding text.

2.07.2.4 Selected Super-Earths

To show the richness in potential super-Earth mineralogy, here, we summarize the characteristics and possible internal compositions of a few selected super-Earths.

CoRoT-7b was the first super-Earth planet to have its radius determined (Léger et al., 2009). The value of this property from transit observations is $1.58 (0.10) R_{\oplus}$ (Bruntt et al., 2010). The mass is uncertain due to the high activity level of the host star, and recent measurements yield $M_P = 5.2 \pm 0.8 M_{\oplus}$ (Bruntt et al., 2010) or $M_P = 7.42 \pm 1.21 M_{\oplus}$ (Hatzes et al., 2011) with nonoverlapping uncertainties. These correspond to average densities of 7.2 ± 1.8 and $10.4 \pm 1.8 \text{ g cm}^{-3}$, respectively. For comparison, the mean density of Earth is 5.5 g cm^{-3} . The densities indicate that the planet has a dominantly rock–metal interior structure (Figure 2). Models to date yield compositions ranging from an Earth-like composition

with a core of $\sim 30\%$ of the mass for the lower-density case to a more Mercury-like composition with a core that is $2/3$ of the total mass for the high-density case (Wagner et al., 2012). In detail, models predict that the density of the mantle increases by a factor of ~ 2.2 – 2.5 from the surface value to the core–mantle boundary (Wagner et al., 2012). The central pressure is estimated to be as high as 2000 GPa in the low-density case and 4000 GPa for the high-density model (Swift et al., 2012; Wagner et al., 2012). The density of the Fe core at the center of the planet is estimated to be $\sim 22 \text{ g cm}^{-3}$ (Léger et al., 2011; Wagner et al., 2012), representing approximately a threefold compression of iron compared with ambient conditions.

CoRoT-7b orbits very closely to its host star (G type) with a semimajor axis of $\sim 0.017 \text{ AU}$. Thus, the surface is expected to be very hot, and as the planet is tidally locked, a large variation in dayside ($\sim 2500 \text{ K}$) and nightside (50 – 75 K) temperatures is expected (Léger et al., 2011). This may result in the formation of a lava ocean on the stellar-facing hemisphere of the planet (Léger et al., 2011). Questions surrounding the origin of CoRoT-7b have also attracted interest. It has been speculated that this planet could be a chthonian planet, resulting from the stripping away of a gas or ice giant's outer layers due to proximity to its host star and leaving behind only the residual central core (Lecavelier des Etangs et al., 2004). However, recent mass-loss models suggest that CoRoT-7b was most likely always a rocky planet (Leitzinger et al., 2011).

Another recently detected planet with similar properties is Kepler-10b. Its radius ($\sim 1.4 R_{\oplus}$) and mass ($\sim 4.6 M_{\oplus}$) yield a high average density ($\sim 8.8 \text{ g cm}^{-3}$) (Batalha et al., 2011). It also orbits a G-type parent star at a close distance ($a = 0.0168 \text{ AU}$). The interior composition is predicted to be Mercury-like, similar to the high-density case for CoRoT-7b (Wagner et al., 2012).

GJ 1214b appears to be intermediate between terrestrial planets such as the Earth and the ice giants Neptune and

Uranus. It has a mass of $6.55 \pm 0.098 M_E$, but its density ($1.87 \pm 0.40 \text{ g cm}^{-3}$) is only $\sim 1/3$ that of the Earth. Possible interior models include a rocky planet with an outgassed atmosphere, a scaled-down version of Neptune (i.e., sub-Neptune, a rocky/icy core with hydrogen-rich atmosphere), or an ice-dominated interior analogous to Jupiter's icy satellites (Rogers and Seager, 2010). In any case, the low density implies that it almost certainly has a significant gas component. A discussion of current understanding of this planet's atmosphere is contained in the succeeding section.

55 Cancri e is a super-Earth orbiting a nearby G8V star with an orbital period of 18 h. It has a mass of $8.37 \pm 0.38 M_E$ and a radius of $2.04 \pm 0.15 R_E$ (Endl et al., 2012; Gillon et al., 2012) yielding a density of $\sim 5.43 \text{ g cm}^{-3}$, similar to the mean density of the Earth. The interior composition has been suggested to be composed of refractory materials (silicates and iron) with an envelope ($>10\%$ by mass) of supercritical water (Demory et al., 2011; Gillon et al., 2012; Winn et al., 2011). As an alternative, the interior may be composed of Fe, C, SiC, and/or silicates without a volatile envelope (Madhusudhan et al., 2012). Figure 7 shows the range of silicate, metals, carbide, and carbon compositions that can satisfy observational data for this planet. Such a carbon-rich composition is plausible if the protoplanetary disk reflected the composition of the host star, which has been reported to be carbon-rich (Delgado Mena et al., 2010). The possibility of carbon-rich planets with interiors dominated by Fe, C, SiC, and/or silicates has previously suggested based on stellar compositional abundances and planetary formation models (Bond et al., 2010; Kuchner and Seager, 2005; Madhusudhan et al., 2011). Planets with carbon-rich interiors represent a potential new regime of interior structure, composition, and evolution compared to planets within our solar system.

2.07.2.5 Super-Earth Atmospheres

Only recently it has become possible to observe the atmospheres of super-Earths. As discussed in Section 2.07.2.2, observing super-Earth atmospheres requires particularly favorable conditions in terms of the stellar hosts, that is, the star has to be either relatively small or particularly bright. Atmospheric observations have been reported for only two super-Earths to date, GJ 1214b (Bean et al., 2010) and 55 Cancri e (Demory et al., 2011, 2012), of which GJ 1214b is by far the most studied. Transmission spectra of the atmosphere of GJ 1214b have not revealed any molecular features over a wide wavelength range ($0.6\text{--}5 \mu\text{m}$). The observed spectra are consistent with either an atmosphere with a high mean molecular weight, implying a small scale height and hence nondetection of molecular features within the precision of the data, or the presence of thick clouds in the atmosphere, which may be hydrogen-rich, thereby masking any molecular features. Limited photometric data are also available for the super-Earth 55 Cancri e, which suggest multiple possible atmospheric compositions, depending on what is assumed for the interior composition. If an Earth-like oxygen-rich interior is assumed, the planet is expected to host a thick envelope of supercritical water of 20% by mass of the planet (Gillon et al., 2012; Winn et al., 2011). However, Madhusudhan et al. (2012) suggested that the planet could be carbon-rich in its interior, in which case available infrared data can be explained by a variety of different atmospheric scenarios, including no atmosphere at all.

As the study of super-Earth atmospheres is still in its infancy, several questions of observational and theoretical significance lay open at the forefront. As alluded to earlier, one of the key questions at the heart of the field concerns distinguishing which super-Earths are Neptune-like and which are Earth-like or have other compositions. Chemical characterization of

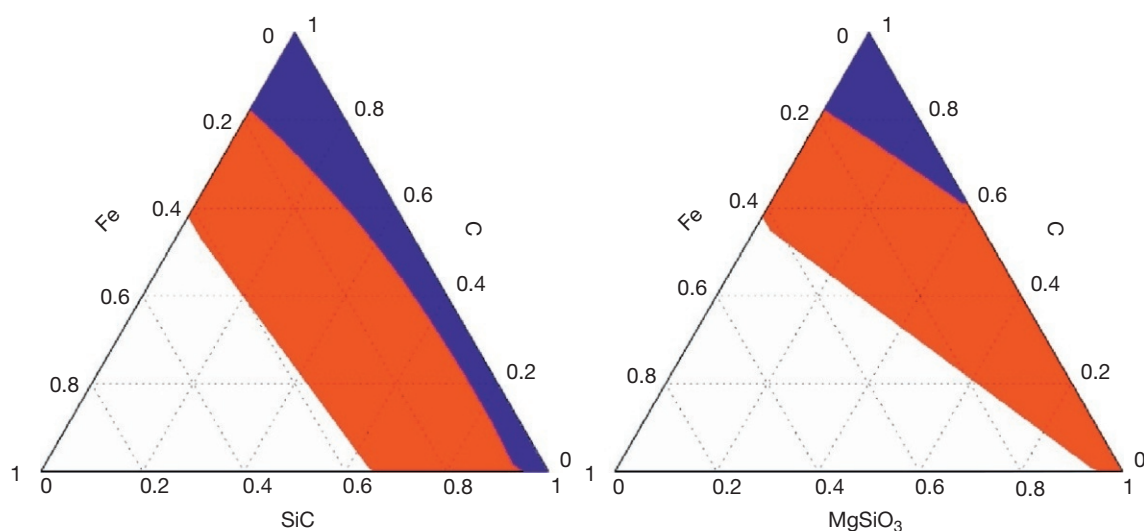


Figure 7 Ternary diagrams showing the range of interior compositions allowed by the mass and radii of 55 Cancri e. Two classes of interior models were considered based on planetesimal compositions predicted by the stellar abundances. (Left) Models composed of Fe, SiC, and C. (Right) Models composed of Fe, MgSiO_3 , and C. In each case, the red and blue contours show the constraints from the two reported values of measured radius for this planet (see Figure 2). The blue contours are subsets of the red contours. The three axes in each case show the mass fractions of the corresponding species. Reproduced from Madhusudhan N, Lee KKM, and Mousis O (2012) A possible carbon-rich interior in super-Earth 55 Cancri e. *Astrophysical Journal Letters* 759(2): L40. <http://dx.doi.org/10.1088/2041-8205/759/2/L40>, with permission.

their atmospheres may be a key step for distinguishing among degenerate compositional models. On the other hand, currently known super-Earths span an extremely wide range in thermochemical surface conditions (Figure 3). As such, the possible atmospheric chemical compositions of super-Earths are also diverse, beyond the gross distinction of H₂-rich versus H₂-poor. While super-Earth atmospheres at the cooler end can host vast complexes of condensates and aerosols (Miller-Ricci and Fortney, 2010; Morley et al., 2013), the hottest of super-Earths can host atmospheres of vaporized refractory species, such as silicate-rich atmospheres (e.g., Schaefer et al., 2012). The extent and nature of volatile content in super-Earth atmospheres is also intricately linked to their evolutionary history. Depending on their original mass, age, stellar properties, and paths of formation and migration, some super-Earths may retain significant envelopes of volatile species such as H₂ or water vapor for a significant fraction of their lives, whereas others would be expected to have lost most of their original atmospheres (e.g., Lopez et al., 2012). Most importantly, the atmospheric compositions of super-Earths are intricately linked to their interior compositions. Traditionally, atmospheres of super-Earths have largely been studied assuming water as the key volatile (Lopez et al., 2012; Rogers and Seager, 2010; Valencia et al., 2007a), motivated by the oxygen-rich composition of the Earth. However, alternate interior compositions may lead to very different atmospheric compositions. For example, carbon-rich super-Earths (e.g., Madhusudhan et al., 2012) may be devoid of significant amounts of water vapor in the atmosphere, as water ice may be chemically inhibited in carbon-rich formation environments. Consequently, understanding the atmospheres and interior mineralogies of super-Earths is a critical step in assessing the phase space of possible compositions for these bodies.

2.07.3 Theoretical and Experimental Techniques for Ultrahigh-Pressure Research

Interpretation of mass–radius relationships for super-Earths requires knowledge of the equation of state (EOS) of planetary materials, and construction of detailed thermal and evolutionary models requires further understanding of a broader range of thermodynamic, rheological, and transport properties. The *P*–*T* conditions of super-Earth interiors (Figures 4 and 5) typically lie above the range of direct laboratory experiments but below the validity of ultrahigh-pressure theoretical EOSs such as the Thomas–Fermi–Dirac (TFD) model (Valencia et al., 2009). This section summarizes the basic theoretical and experimental approaches now being used to explore and predict the relevant material properties under super-Earth conditions.

2.07.3.1 Theoretical Methods

Planetary materials are now routinely studied by means of first-principles or *ab initio* quantum mechanical simulations. These methods refer to calculations based on the many-body Schrödinger equation, where empirically determined parameters are not used; thus, these methods are based solely on the properties of electrons and nuclei with no input from

experiment. Although approximations to these methods are necessary in order to efficiently solve the equations, these approximations are well tested for a wide range of materials and conditions.

Density functional theory (DFT) is arguably the most successful first-principles method to study the high-pressure (ground-state) behavior of terrestrial materials and has been described in detail elsewhere (e.g., Gillan et al., 2006; Wentzcovitch and Stixrude, 2010; Chapters 2.08 and 2.11). Approximations such as the local density approximation (LDA) and generalized gradient approximation (GGA) are used in practice with DFT to treat the exchange and correlation between the electrons in the computation of energies. To include high-temperature effects requires more demanding computations than for ground-state (i.e., zero-temperature) simulations because at high temperature, the free energy plays the essential role, and an accurate calculation of this requires expensive sampling of phase space.

DFT calculations have been extensively tested against experiment at lower pressures, and the successes and limitations of the method are well established. For many planetary materials, the accuracy of LDA and GGA is typically ~1–2% for bond lengths and unit cell dimensions, ~5% for vibrational frequencies, and ~15% for elastic constants (Oganov et al., 2013). At the extreme conditions of exoplanets and giant planet cores, DFT methods are not well tested as yet. Current implementations of DFT use pseudopotentials, which are effective potentials that describe the valence electrons but exclude core electrons. Pseudopotential calculations may not be accurate when compressions are sufficiently high such that core electrons begin to participate in chemical bonds (Umemoto et al., 2006a). In such cases, the use of all-electron methods or pseudopotentials that include core orbitals would be necessary. One study that compared Fe pseudopotentials to all-electron calculations at super-Earth pressures yielded identical results with the two methods, supporting the continued reliability of pseudopotential methods (Cottenier et al., 2011).

For materials at moderate temperatures (i.e., less than the Debye temperature), a generally useful approach is the quasi-harmonic approximation (QHA), where the potential energy of the crystal is expanded to second order in the displacement of the atoms from their equilibrium positions. This has been shown to work well for important Earth minerals such as ferropericlase (Mg,Fe)O and Mg-silicate perovskite (Mg,Fe,Al)SiO₃, although there are exceptions such as Ca-silicate perovskite, CaSiO₃, due to its anharmonicity (Wentzcovitch et al., 2010). The QHA method has been applied to determine phase diagrams of MgSiO₃, SiO₂, CaSiO₃, etc. (Tsuchiya and Tsuchiya, 2011; Umemoto and Wentzcovitch, 2011; Wu et al., 2011), under super-Earth interior conditions as discussed in the succeeding text, but it has not yet been well tested through comparison with experiment at ultrahigh pressures.

For highly anharmonic solids and liquids or harmonic solids at higher temperatures, molecular dynamics (MD) or Monte Carlo (MC) techniques are used to sample phase space. For MD, the approach is to move the ions according to the Newton's equations of motion (e.g., $F_i = m_i dv_i/dt$) where each atom *i* has a mass *m*, velocity *v*, and force *F* acting upon it. With appropriately small time steps (e.g., <1/20th of a

vibrational period), one can approximate the solution of the equation of motion (Verlet, 1967). MD simulations are attractive because they also provide information on dynamics and can be used to simulate diffusion behavior, viscosities, and electrical and transport properties, all of which are important for understanding the interiors and evolution of exoplanets (Swift et al., 2012). MC techniques, such as path integral MC, are among the most accurate finite-temperature quantum simulation methods available as they include all correlation effects and track all electrons and the nuclei (Ceperley, 2010). They are efficient at high temperatures ($>\sim 5000$ K) and can provide a good description of matter reaching up to a fully ionized plasma state. At lower temperatures, the computations become prohibitively expensive, and thus, it becomes more efficient to use a ground-state simulation method such as quantum MC (Ceperley, 2010).

For the mineralogy expected for super-Earths, these high-temperature methods have not been widely employed yet at super-Earth conditions (e.g., Seager et al., 2007) especially as compared to models for the interiors of Jupiter (or larger)-sized planets where the most abundant elements, H and He, are very sensitive to temperatures (e.g., Militzer and Hubbard, 2009). For heavier materials, the effect of temperature is less important for the EOSs and the resulting mass-radius relationships that are computed from them. High-temperature studies, however, are important for determining the thermal state of a planet and its thermochemical and thermomechanical evolution.

An important recent stride in first-principles theory is the development of approaches for crystal structure prediction that do not require candidate structures as input. This can be particularly useful under the extreme pressures of exoplanets where information on possible crystal structures may be uncertain or incomplete. *Ab initio* crystal structure prediction requires methods to search through the potentially large space of possible structures to locate the ground-state structure in an efficient manner. Approaches developed for this include evolutionary algorithms (Glass et al., 2006) and random structure searching (Pickard and Needs, 2011). Applications of these methods so far at exoplanet-relevant pressures include studies of carbon (Martinez-Canales et al., 2012), iron (Pickard and Needs, 2009), and the Mg–O system (Zhu et al., 2013). It is expected that many more applications of these approaches will be forthcoming in the future.

2.07.3.2 Experimental Techniques

High-pressure experimental techniques can be divided into static and dynamic methods. For achieving high static pressures, the diamond anvil cell (DAC) provides the widest pressure–temperature coverage. Dynamic experiments fall into two categories: shock compression and ramp compression. Shock compression techniques are well established and have been applied to many types of materials. Ramp compression is an emerging technique with the potential to cover regions of P – T space not easily accessed with either DACs or conventional shock methods. Each of these techniques is discussed in turn in this section.

2.07.3.2.1 Diamond anvil cell

The DAC is the most widely used device for high-pressure research (see Chapter 2.11). In DAC experiments, a small

(~ 10 – 100 μm) sample is compressed between two gem-quality diamonds. The highest reported pressure achieved in the DAC to date is 640 GPa (Dubrovinsky et al., 2012), but the vast majority of DAC measurements are carried out at less than 200 GPa. The sample can be heated while under pressure using resistive or laser heating techniques allowing temperatures up to several thousand Kelvin to be achieved. Recently, the highest combined P – T conditions yet achieved in the laser-heated DAC, approaching 400 GPa and 6000 K, have been reported (Tateno et al., 2010).

The transparency of diamond in the visible, infrared, and x-ray portions of the spectrum enables application of a variety of optical and x-ray techniques under *in situ* high-pressure conditions with this device. Static compression studies using the DAC have thus enabled exploration of a wide range of phenomena in materials at pressures of up to ~ 200 GPa and temperatures ranging from near zero to several thousand Kelvin. The study of crystal structures, phase transformations, EOSs, and other thermodynamic properties is a major focus of static high-pressure studies (Duffy, 2005). Significant changes in atomic bonding occur at high pressures, and materials also undergo major changes in mechanical and rheological properties.

At present, the DAC can sample most of the P – T range expected in the Earth's interior. Further development of diamond cell technology promises to expand the available pressure range further and, equally importantly, expand the types and accuracy of experiments that can be performed. Yet, it is unlikely that DAC techniques will be able to reach the full range of P – T conditions that are expected to be encountered in super-Earth exoplanets (Figures 4 and 5). For higher-pressure experiments, dynamic compression techniques are required.

2.07.3.2.2 Dynamic compression

Shock compression is the major technique used for achieving high pressures dynamically. Shock wave studies have wide applications to understanding high-pressure behavior, impact phenomena, and the high-strain rate response of all types of materials. A review of shock compression studies for planetary applications is given by Ahrens (1987) and in Chapter 2.16. A shock wave is a large-amplitude mechanical wave across which pressure, density, particle velocity, temperature, and other material properties change nearly discontinuously (Boslough and Asay, 1993; Figure 8). Shock waves propagate with supersonic velocity (relative to unshocked material), and unlike acoustic waves, their velocity is amplitude-dependent. For shock waves that propagate in a steady manner, the Rankine–Hugoniot equations express conservation of mass, momentum, and energy across the shock discontinuity:

$$\frac{\rho}{\rho_0} = \frac{U_s}{U_s - u_p} \quad [6]$$

$$P - P_0 = \rho_0 U_s u_p \quad [7]$$

$$E - E_0 = \frac{1}{2}(P + P_0)(1/\rho_0 - 1/\rho) \quad [8]$$

where U_s is the shock wave velocity, u_p is the particle velocity, E is the specific internal energy, and the subscript 0 refers to the initial unshocked state.

Shock compression is highly irreversible, and a substantial portion of the energy in a shock wave goes into raising the

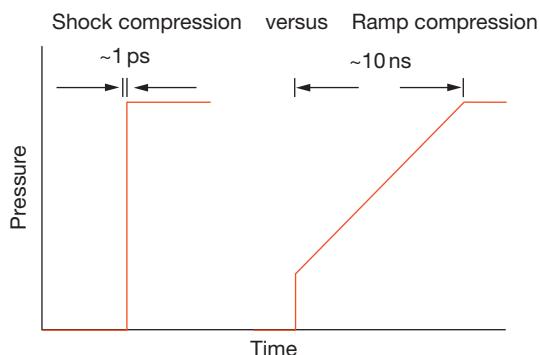


Figure 8 Schematic illustration of a shock wave (left) and a ramp wave (right). The ramp loading wave consists of an initial shock, followed by ramp loading to higher pressures. Modified from Nellis WJ (2007) *Adiabatic-reduced isotherms at 100 GPa pressures. High Pressure Research* 27: 393–407, with permission.

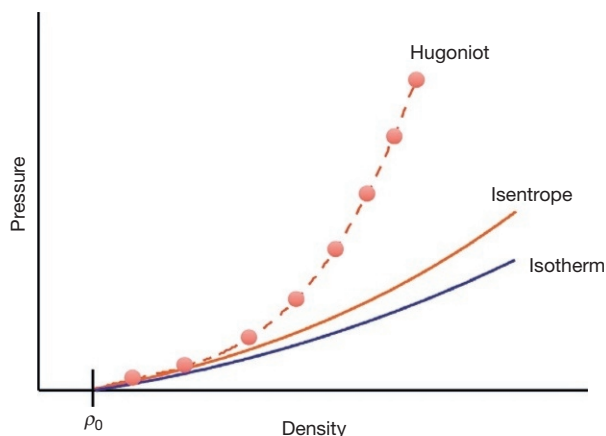


Figure 9 Thermodynamic curves for high-pressure experiments illustrating the isotherm (diamond anvil experiments), isentrope (approached by ramp compression), and Hugoniot (shock wave experiments). Ramp compression can sample the P – T – ρ space between the principal isentrope and the shock Hugoniot curve.

entropy of the material. As a result, temperature rises with compression. At low pressure, the temperature rise is modest, but temperature increases strongly at higher compression. Shock heating ultimately leads to melting of solids. This typically occurs at pressures of ~ 100 – 300 GPa for refractory materials of planetary interest, so shock wave experiments at ultrahigh pressures are probing high-temperature liquid states. There is also a limiting value to the achievable compression as the shock energy becomes increasingly partitioned into additional heating of the sample rather than compression (Johnson, 1999).

Standard shock wave techniques use gas guns to accelerate a flyer plate to several km s^{-1} , which generates a shock wave when impacting a sample. The shock and particle velocities are measured using laser interferometry or a streak camera. This enables the thermodynamic state (P , ρ , and E) to be constrained through application of the Rankine–Hugoniot equations (eqns [6]–[8]). As shown in Figure 9, the Hugoniot curve is the locus of final states achieved with a single shock

from a given set of initial conditions (note that it is not the thermodynamic path followed by the shocked material). Each shock compression experiment thus determines a single datum on the Hugoniot curve. An important consequence of eqns [6]–[8] is that an independent pressure calibrant is not required for shock experiments as pressure is determined from the measured flow variables and conservation of momentum. For this reason, reduced shock wave data are commonly used for the calibration of pressure standards in static DAC experiments (Nellis, 2007). Note also that the Hugoniot equations do not constrain temperature directly, but this can be obtained in many cases by a measurement of the thermal radiation emitted by the shocked sample (Eggert et al., 2009; Luo et al., 2004; Svendsen and Ahrens, 1987).

In addition to gas-gun experiments, high-powered lasers and magnetic pulsed power facilities are increasingly being used for dynamic loading of materials. There are several large laser facilities worldwide including the VULCAN laser, an eight-beam 2.5 kJ Nd: glass laser at the Rutherford Appleton Laboratory (Danson et al., 1998; Ross et al., 1981); the Omega laser, a 60-beam 30-kJ Nd: glass laser at the University of Rochester (Boehly et al., 1997); and the National Ignition Facility (NIF) at Lawrence Livermore National Laboratory, which is a 192-beam laser with up to 2 MJ of laser energy (Moses, 2011). In experiments at these facilities, irradiance from a short ($\sim \text{ns}$), intense laser pulse causes the surface of the sample under study to ablate, and the plasma blowoff creates a strong compression wave that propagates through the sample (Figure 10). The Z machine at Sandia National Laboratory is a pulsed power accelerator that can produce currents to 20 MA and magnetic fields to 10 MG that is also capable of ultrahigh-pressure dynamic compression experiments (Matzen et al., 2005).

Thermodynamic paths of interest for compressed states of matter are compared in Figure 9. The isotherm is the pressure–volume response of the material at constant temperature. The 300 K isotherm can be measured in a DAC experiment, whereas the 0 K isotherm or cold curve can be obtained from ground-state DFT calculations. The Hugoniot is the result of adiabatic, but highly irreversible shock compression, resulting in a high-temperature shock state and a pressure offset from the isotherm that increases with compression. At lower pressures, where shock heating is small, the Hugoniot is close to the isentrope (neglecting strength effects), but these diverge increasingly at higher pressures. The isentrope is the thermodynamic path that corresponds to continuous compression that is both adiabatic and reversible. In this case, there is a modest temperature rise resulting from compression, and the isentrope lies above the isotherm.

An alternative dynamic loading technique that is attracting interest for the study of materials under exoplanetary conditions is ramp loading (Bradley et al., 2009; Lorenz et al., 2005). In this case, the material is dynamically loaded at a slower rate corresponding to rise times of 10–100 ns, compared with ~ 1 ps for shock compression (Figure 8). These loading rates are sufficiently slow that isentropic, rather than shock, compression is produced at least ideally. A ramp compression wave can be viewed in the limit where the compression wave is broken up into a series of weak shocks that isentropically compress the sample up to the final pressure. In reality, there

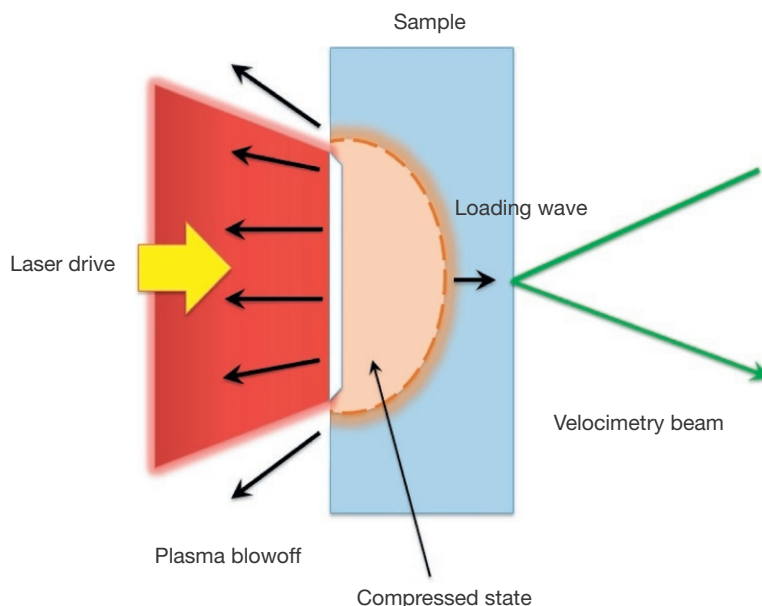


Figure 10 Schematic diagram illustrating laser-based dynamic compression experiment.

will be irreversible work and heating due to dissipative processes such as defect generation and motion, and so the term ‘quasi-isentropic’ is sometimes used.

Ramp loading has a number of potential advantages for studying materials at ultrahigh pressures. The lower entropies achieved upon ramp loading mean that the amount of heating will be much less than for shock compression and, consequently, solids can be compressed to very high pressures without experiencing melting. It enables access to the wide range of P - T states that lie between the isotherm and the Hugoniot (Figure 9). In addition, ramp loading allows measurement of a continuum of pressure-density states along the load curve, unlike steady shock compression, which yields only one point on the Hugoniot per experiment. However, ramp loading conditions can be challenging to maintain experimentally because sound velocities normally increase with pressure, and large-amplitude pressure waves thus tend to steepen into shocks.

Ramp compression can be carried out using various techniques including projectile impact methods, pulsed magnetic sources, and high-powered pulsed lasers as described earlier for shock compression. Laser ramp compression experiments on the 30 kJ Omega laser have probed materials such as diamond, iron, and magnesium oxide to pressures as high as 900 GPa (Bradley et al., 2009; Coppari et al., 2013; Wang et al., 2013). x-Ray diffraction can also be carried out in ramp loading experiments (Rygg et al., 2012). In these experiments, a thin powder sample, held between diamond plates, is ramp- or shock-compressed using a laser source. Wave reverberations between the sample and diamond plates create a state of uniform pressure in the sample. Measurement of the velocity history of the rear diamond, together with the known EOS of diamond (Bradley et al., 2009), allows determination of the pressure history of the thin sample. A second set of lasers are used to irradiate a thin foil creating a quasimonochromatic x-ray source. The x-rays impinge on the sample through a collimating pinhole, allowing a diffraction pattern to be

recorded on image plates surrounding the sample. x-Ray diffraction data on MgO have been measured to 900 GPa by this technique (Coppari et al., 2013). This provides direct determination of the pressure-density states and provides a means to directly determine crystal structures under dynamic loading at extreme conditions for the first time.

2.07.4 Equations of State

The EOS is a relationship between the pressure, temperature, and density of a material in thermal equilibrium. The $\rho(P, T)$ EOS is one of the most important high-pressure material properties and an essential component of interior structure models for exoplanets as discussed earlier (eqns [1]–[3]). For the range of plausible masses of super-Earths (1–10 M_E), the interior pressures and temperatures are expected to be very high (to ~ 4000 GPa, 10 000 K) (Figures 4 and 5) and require accurate characterization of the EOS over large compression. The various experimental and theoretical techniques that can be used for EOS measurements have been discussed earlier. Experimental compression data are typically fit using semiempirical EOS such as the Birch–Murnaghan or the Vinet equation. The Birch–Murnaghan EOS (Birch, 1952) is widely used in geophysics and is derived from a power series expansion of the free energy in finite strain. To the third order in Eulerian strain, the Birch–Murnaghan equation is given by

$$P = \frac{3}{2} K_0 \left[\left(\frac{V_0}{V} \right)^{7/3} - \left(\frac{V_0}{V} \right)^{5/3} \right] \left\{ 1 + \frac{3}{4} [K'_0 - 4] \left[\left(\frac{V_0}{V} \right)^{2/3} - 1 \right] \right\} \quad [9]$$

where V is the volume, K is the bulk modulus, K' is the pressure derivative of the bulk modulus, $\partial K / \partial P$, and the subscript 0 refers to ambient-pressure conditions. Parameters of the EOS are typically fit using experimental data from DAC

experiments or shock compression data appropriately corrected for thermal effects. Uncertainties in the Birch–Murnaghan EOS arise from truncation of the power series (typically to the third order in strain) and the choice of finite strain measure. This equation has been used to represent the EOS in several studies of exoplanet interiors to date (Seager et al., 2007; Sotin et al., 2007; Valencia et al., 2006).

Another EOS widely used for solids is the Vinet equation (Vinet et al., 1986, 1989):

$$P = 3K_0 \frac{1-X}{X^2} \exp \left[\frac{3}{2} (K'_0 - 1)(1-X) \right] \quad [10]$$

where $X = (V/V_0)^{1/3}$. This equation is based on a Rydberg interatomic potential and is expected to be applicable to solids with a wide range of bonding types. Comparisons of EOSs with experimental and theoretical data over wide ranges of compression support the reliability of the Vinet equation for best characterizing experimental data (Cohen et al., 2000). This equation or a modified form of it has also been adopted for exoplanet interior modeling (Valencia et al., 2007b; Wagner et al., 2012). Examples of EOSs for major potential components (Fe, MgSiO₃, and H₂O) of super-Earths are shown in Figure 11.

The effects of temperature on the EOS can be included using one of several thermal models (Duffy and Wang, 1998). A particularly useful approach is the Mie–Grüneisen–Debye formulation, which uses a thermal correction to the isothermal EOS that accounts for lattice vibrations with a cutoff frequency corresponding to the Debye frequency (Jackson and Rigden, 1996). The total pressure is divided into a cold term, P_c , and a thermal term, P_{th} :

$$P(V, T) = P_c(V) + P_{th}(V, T) \quad [11]$$

The reference isotherm, P_c , is given by an EOS such as the Vinet or Birch–Murnaghan equation. The thermal pressure is obtained from

$$P_{th} = \frac{\gamma}{V} [E(T, \theta) - E_c(T_c, \theta)] \quad [12]$$

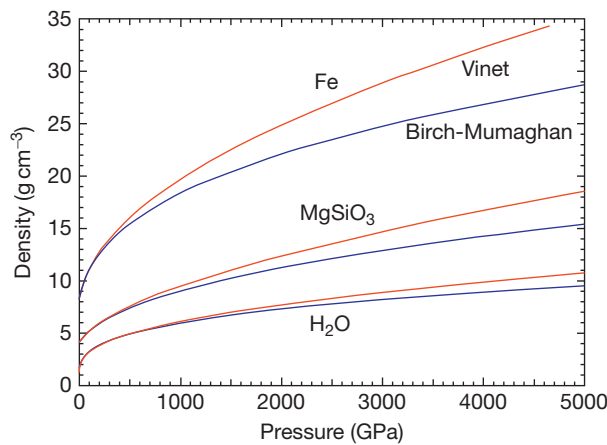


Figure 11 Room-temperature equations of state for representative planetary materials. Blue and red curves show difference in density resulting from extrapolations of experimental data using the Birch–Murnaghan and Vinet equations, respectively. Equation of state parameters for each material are from Fe (Dewaele et al., 2006), MgSiO₃ (Lundin et al., 2008), and H₂O (Somayazulu et al., 2008).

where E is the thermal energy, γ is the Grüneisen parameter, and θ is the Debye temperature. The thermal energy can be calculated from the Debye model:

$$E(T, \theta) = 9nRT \left(\frac{T}{\theta} \right)^3 \int_0^{\theta/T} t^3 dt / (e^t - 1) \quad [13]$$

where n is the number of atoms per formula unit and R is the gas constant. The Debye temperature and Grüneisen parameters are functions of volume according to

$$\gamma(V) = \gamma_0 \left(\frac{V}{V_0} \right)^q \quad [14]$$

and

$$\theta = \theta_0 \exp [(\gamma_0 - \gamma(V))/q] \quad [15]$$

where q controls the volume dependence of γ . The complete Mie–Grüneisen–Debye equation thus requires specification or determination of six parameters: V_0 , K_0 , K'_0 , γ_0 , θ_0 , and q . The thermal parameters can be obtained from P–V–T experimental data or from measurements or estimates from elasticity or other thermodynamic data (Duffy and Wang, 1998; Jackson and Rigden, 1996). Under super-Earth conditions, the effect of temperature on density is considered to be of second-order importance compared to the pressure effect (Seager et al., 2007; Valencia et al., 2007a), so the thermal EOS only plays a minor role in determining the mass–radius relationship. The thermodynamic properties, however, are essential for thermal and evolutionary models of exoplanets (e.g., Wagner et al., 2012). The Grüneisen parameter plays a particularly important role. Interior temperatures in super-Earths are expected to be sufficiently hot that thermal convection will be a dominant heat transport mechanism. For a convecting super-Earth, the adiabatic temperature gradient, $(\partial T / \partial r)_s$, is given by

$$\left(\frac{\partial T}{\partial r} \right)_s = - \frac{\rho g \gamma T}{K_s} \quad [16]$$

where r is the planetary radius, g is gravitational acceleration, and K_s is the adiabatic bulk modulus. While absolute temperatures of a planet will depend on many factors as discussed previously, the adiabatic gradient determines the slope of the temperature profile for convecting regions in the mantle and core. The Grüneisen parameter is also used to estimate the melting temperatures of mantle and core materials through Lindemann’s law (Gaidos et al., 2010; Poirier, 2000; Stamenkovic et al., 2011; Valencia et al., 2006).

Another P–V–T EOS that has been used for modeling exoplanets is ANEOS (Thompson, 1990; Thompson and Lauson, 1972), which is a long-standing EOS widely used in the modeling of shock experiments and impact events. It uses a thermodynamically consistent Helmholtz free energy formulation that extrapolates to the Thomas–Fermi limit (discussed in the succeeding text) at ultrahigh pressures. ANEOS is largely based on experimental shock wave data with thermal corrections using the Grüneisen parameter. An advantage of this EOS is the correct asymptotic behavior at very high pressures, but potential limitations include its approximate treatment of phase transitions, large thermal corrections from Hugoniot conditions to the high-P, lower-T conditions of planetary interiors, and limited options for modeling geological materials (Melosh, 2007). However, a

recent comparison of EOSs for exoplanet applications concluded that ANEOS does work well in the pressure regime of particular interest for exoplanet interiors (Grasset et al., 2009).

Since EOSs must be extrapolated to very high pressures beyond the range of experiments, their reliability at high compressions must be evaluated. Stacey (2000) suggests that K'_{∞} , the asymptotic limit of the pressure derivative of the bulk modulus as pressure goes to infinity, can be used as an additional criterion for evaluating EOSs. A constraint on K'_{∞} obtained from thermodynamic relationships at this infinite limit can be used to modify the Vinet equation to be consistent with this limit (Stacey and Davis, 2004). At extreme pressures, all materials are expected to reach the Thomas–Fermi limit of a free electron gas with embedded nuclei. In this case, the pressure of the degenerate electron gas is calculated using the TFD approximation. TFD-based electronic structure theory (Salpeter and Zapolsky, 1967) is expected to provide an adequate EOS at pressures exceeding ~ 10 TPa (Grasset et al., 2009; Seager et al., 2007). Uncertainty in the EOS therefore is primarily in the regime between 0.2 and 10 TPa, beyond the limit of most experimental data and below the validity of the high-density, fully ionized limit. Existing EOSs for planetary materials can differ by ~ 20 – 30% in the 100 GPa to 10 TPa range (Baraffe et al., 2008). Comparisons of models with different EOSs suggest that uncertainty in EOS translates into an uncertainty in radius of ~ 2 – 3% for a given mass planet (Fortney et al., 2009; Wagner et al., 2011). As this uncertainty is comparable to the expected precision in future telescope observations of transits, reducing EOS uncertainty is needed to make structure models more accurate.

2.07.5 Mineralogy at Super-Earth Interior Conditions

2.07.5.1 Composition of Super-Earths

The bulk composition of a planet should reflect that of its host star as modified by planet-forming processes within the protoplanetary disk. In general, a wide range of bulk compositions for terrestrial-type planets should be possible, in principle. The mineralogy of terrestrial super-Earths can be modeled assuming an Earth-like composition as a starting point. The composition of Earth is dominated by O, Fe, Mg, and Si with lesser amounts of Ca and Al (McDonough and Sun, 1995). The Earth's interior consists of a mantle composed of Mg-rich silicates and oxides overlying a metallic Fe core, with other species in minor amounts (see Chapters 2.03, 2.06, and 10.02).

Measured photospheric stellar abundances of the elements provide constraints on both internal and atmospheric compositions of exoplanets as well as insights into what characteristics of protoplanetary clouds favor planetary formation (Delgado Mena et al., 2010). The Mg/Si, Fe/Si, and C/O ratios are important for determining the mineralogy and structure of terrestrial planets. The Mg/Si ratio will control the relative abundance of the major silicates such as pyroxenes (Mg/Si = 1) and olivine (Mg/Si = 2). The solar and bulk Earth Mg/Si values are close to one (Asplund et al., 2009; Kargel and Lewis, 1993; McDonough and Sun, 1995). Photospheric measurements of planet-hosting stars show a range of Mg/Si values ranging from ~ 0.7 to ~ 1.4 (Delgado Mena et al., 2010). In simulations of planetary formation that included variable

chemical composition in the protoplanetary disk, terrestrial planets with variable compositions, some very different from Earth, were found (Bond et al., 2010). Models of systems with low Mg/Si ratios yield planets that are Mg-depleted compared to Earth and are formed from silicates such as pyroxenes and feldspars (Carter-Bond et al., 2012a). However, studies of the relationship between solar abundances, meteorites, and Earth bulk compositions have shown that the relationship between planetary compositions and stellar abundances is complex (Drake and Righter, 2002).

The bulk Fe/Si ratio is an important parameter for determining the size of the metallic core in a terrestrial exoplanet. Values of core mass fraction used in typical models to date are based on analogy to our solar system and range from Earth-like ($\sim 33\%$) to Mercury-like ($\sim 66\%$), while end-member models ranging from pure core to a silicate-only coreless planet are useful for delineating the range of mass–radius space potentially occupied by rocky planets. The core mass fraction will depend not only on bulk Fe content but also on core formation processes that partition Fe between mantle and core (Elkins-Tanton and Seager, 2008). It may also be affected by loss of a planet's mantle due to large impacts or evaporation due to stellar irradiation. For planets of our solar system, the Mg# (=molar Mg/Mg + Fe) of the mantle is known for only Earth and Mars and ranges between 0.7 and 0.9. The distribution of Fe between mantle and core has little overall effect on the mass–radius relationship (Elkins-Tanton and Seager, 2008; Fortney et al., 2009).

The presence of water or other hydrous phases in a terrestrial-type planet is of particular interest as an essential component of habitability. The presence of water can also affect melting behavior and rheology and may affect the likelihood of plate tectonics (Korenaga, 2010). Migration of giant planets may greatly increase the efficiency of delivery of water and hydrous phases to growing terrestrial planets even promoting formation of ocean planets and wet Earths (Carter-Bond et al., 2012b). Close proximity to the host star, on the other hand, can lead to intense heating, which would be expected to strip volatiles from the planet.

Long-lived radioactive elements (^{40}K , ^{232}Th , ^{235}U , and ^{238}U) play an important role as internal heat sources in the Earth, controlling internal temperatures and thermal evolution. The amount of internal heating relative to basal heating in the mantle will affect both internal and surface dynamics (van Heck and Tackley, 2011). Most models of extrasolar planets to date have assumed chondritic abundances of these elements (Tachinami et al., 2011), but the range of possible variability is poorly constrained. Ice-rich planets may be significantly cooler in the interior compared to rocky planets of the same mass due to reduced abundance of radioactive elements (Sotin et al., 2007).

The C/O ratio is a chemical parameter that controls the distribution of Si among oxides and carbides (Bond et al., 2010). Under equilibrium conditions in the innermost region of the protoplanetary disk, a C/O value < 0.8 leads to interiors dominated by silicates (Figure 12). When the C/O ratio is > 0.8 , Si exists as SiC with additional C also present. Further out in the disk, silicates dominate but the resulting planets can be carbon-rich. The types of rocky planets that may form under high C/O ratios have been classified as carbon planets

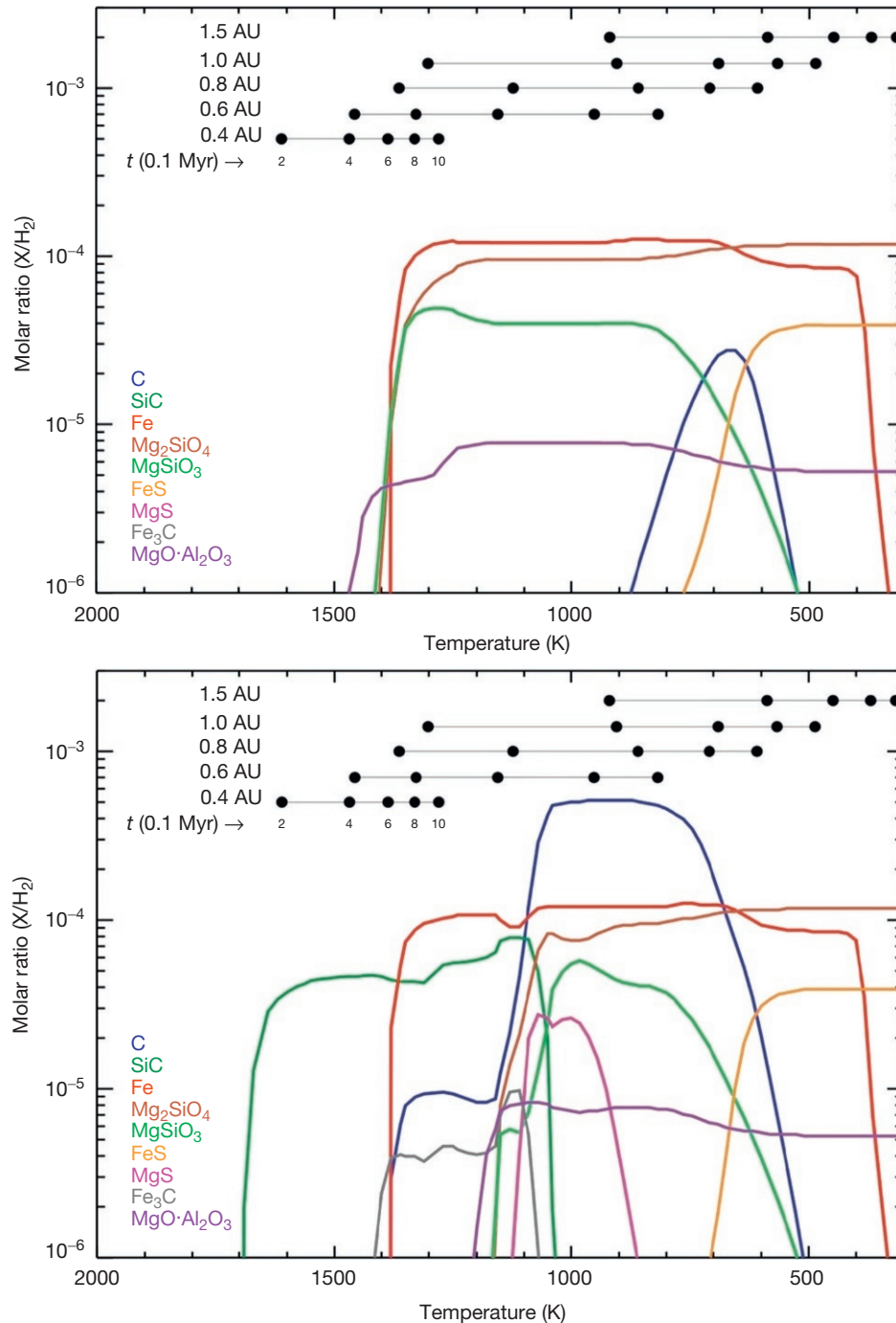


Figure 12 Chemical composition of refractory condensates expected in the protoplanetary disk of the Sun (C/O ratio = 0.54) (top) and of the 55 Cancri system (C/O ratio = 1.12) (bottom). The colored curves show molar mixing ratios of the major species, shown in the legend, in thermochemical equilibrium as a function of temperature in the protoplanetary disk midplane. A representative pressure of 10^{-4} bar is assumed. The elemental abundances of the host star (Carter-Bond et al., 2012b; Delgado Mena et al., 2010) are assumed as initial conditions, and the equilibrium computations were performed using thermochemical software (HSC Chemistry). The black filled circles at the top of the figure show the temperatures of the disk at different orbital separations and ages. Reproduced from Madhusudhan N, Lee KKM, Mousis O (2012) A possible carbon-rich interior in super-Earth 55 Cancri e. *Astrophysical Journal Letters* 759(2): L40. <http://dx.doi.org/10.1088/2041-8205/759/2/L40>, with permission.

(Kuchner and Seager, 2005). A wide range of C/O values have been observed in the photospheric abundances of exoplanet host stars with about one-third of planet-hosting stars having C/O values > 0.8 (Delgado Mena et al., 2010; see also Petigura and Marcy, 2011). On the other hand, some recent studies

have suggested that previous determinations of high C/O in stars could have been overestimated due to systematic errors in estimating the C and O abundances and that carbon-rich main-sequence stars, and hence carbon planets, would be rare (Fortney, 2012; Nissen, 2013).

2.07.5.2 Crystal Structures and Phase Transitions in Minerals at Ultrahigh Pressures

The Earth's mantle extends to a depth of ~ 2900 km and reaches a maximum pressure of ~ 135 GPa (Dziewonski and Anderson, 1981). The upper mantle above 660 km depth is composed mainly of the minerals olivine, pyroxene, and garnet. These minerals undergo a series of phase transitions to denser structures under upper mantle conditions. The major discontinuity at 660 km depth is due to a series of phase transitions culminating in formation of (Mg,Fe)SiO₃ perovskite and (Mg,Fe)O ferropericlase, the two most abundant phases in the lower mantle. Mg-perovskite undergoes a further transformation to the CaIrO₃-type postperovskite structure near the base of the mantle, a few hundred km above the core. The other main mineral of the lower mantle is CaSiO₃ perovskite. The composition of the bulk of the lower mantle, by volume, is expected to be about 70% Mg-perovskite, 20% ferropericlase, and 10% Ca-perovskite (see Chapter 2.03).

The Earth's core accounts for approximately one-third of Earth's mass. Cosmochemical and geophysical evidence indicates that the core not only is mostly iron but also contains Ni and about 10% by mass of a lighter element. The candidates for the major light element of the core are S, O, Si, C, and H, but it is not yet certain which of these is dominant. The core is divided into a small, solid inner core (about 2% of Earth's total mass) and a larger, liquid outer core. The inner core grows slowly over time as the Earth cools. The inner core contains fewer light elements than the outer core, and thus, the composition of the outer core is becoming slowly enriched with lighter elements over time as the inner core grows. This partitioning of lighter elements during inner core crystallization is an important contributor to the driving forces for convective motion of the outer core fluid from which the Earth's

magnetic field is generated. For more details on the core, see Chapter 2.06.

The internal mineralogy of super-Earths will depend on the composition of each planetary layer and pressure and temperature. Here, we review the current understanding of mineralogy and crystal structures of likely phases of relevance. For terrestrial super-Earths, we focus on simple oxides and silicates: MgO, FeO, CaO, Al₂O₃, SiO₂, and MgSiO₃ (Figure 13). Properties of the end-member oxides are an important starting point to understand solid solution, solubility, and dissociation reactions in plausible mineral assemblages. Even for these simple compositions, the phase diagrams are only beginning to be explored at the high P - T conditions characteristic of super-Earth and exoplanet interiors. The behavior of Fe and Fe alloys relevant to the high-pressure conditions expected in super-Earth cores will also be reviewed. The behavior of carbon, H₂O, and other ices is also relevant given the possible range in super-Earth composition extending from terrestrial to Neptune-like planets. C and H₂O are, of course, of special interest due to their importance for addressing questions of habitability and the existence of life. The behavior of all these materials at ultrahigh pressures is not only of interest for super-Earths but also relevant to understanding the cores of giant planets (Chapter 10.16), both in our solar system and beyond.

2.07.5.2.1 MgO

MgO (periclase) is the end-member of the (Mg,Fe)O solid solution. Its high-pressure behavior has attracted much attention due to its simple structure, wide stability field, and geophysical importance. MgO crystallizes in the B1 rock-salt structure, and static compression experiments have shown that the B1 phase remains stable to at least 250 GPa

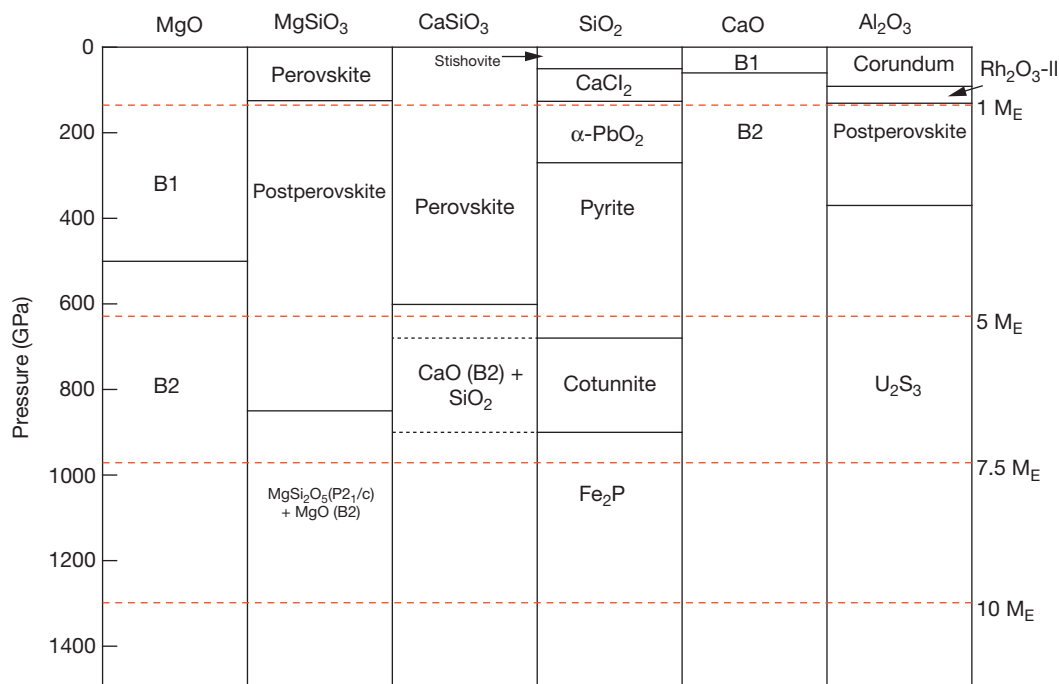


Figure 13 Phase transitions in selected terrestrial mantle constituents at ultrahigh pressures. Red dashed lines show expected core-mantle boundary pressure for terrestrial super-Earths of different sizes based on the model of Wagner et al. (2012).

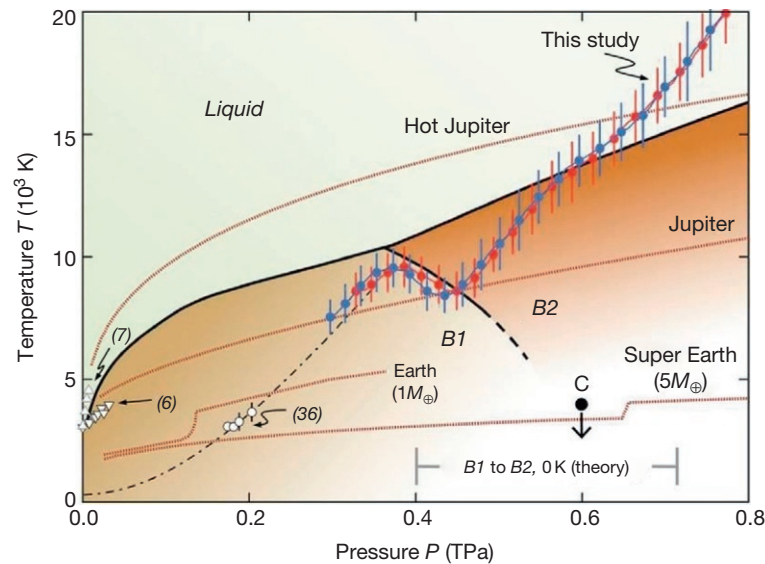


Figure 14 Phase diagram of MgO. Filled red and blue circles and corresponding curves are the shock pressures and temperatures from laser experiments. Brown lines show expected P - T paths for Earth, a $5 M_E$ super-Earth, Jupiter, and a hot Jupiter. The melting curve and B1–B2 phase transition boundary are also indicated. The filled circle labeled C shows the pressure and upper bound temperature for the B1–B2 transition from ramp compression x-ray diffraction experiments (Coppari et al., 2013). Adapted from McWilliams RS, Spaulding DK, Eggert JH, et al. (2012) Phase transformations and metallization of magnesium oxide at high pressure and temperature. *Science* 338(6112): 1330–1333. <http://dx.doi.org/10.1126/science.1229450>, with permission.

(Dorfman et al., 2012; Duffy et al., 1995). Experimental and theoretical constraints on the MgO phase diagram are summarized in Figure 14. Theoretical calculations predict a transformation to the B2 CsCl-type structure with an increase in Mg coordination from 6 to 8 around 400–600 GPa at 0 K (Alfe et al., 2005; Belonoshko et al., 2010; Karki et al., 1997a; Mehl et al., 1988; Oganov et al., 2003; Strachan et al., 1999). A negative Clapeyron slope is predicted theoretically for this phase boundary (Belonoshko et al., 2010; Oganov et al., 2003; Strachan et al., 1999). Ab initio random structure searching has been applied to MgO over 1000–4000 GPa, and no other structure was found to be competitive in enthalpy with the CsCl structure at 0 K (Wilson and Militzer, 2012). Theoretical DFT calculations have also predicted that solid MgO metallizes at 0 K at very high pressures (2100 GPa) (Oganov et al., 2003).

Shock compression work on MgO has reached pressures as high as 1400 GPa (Fat'yanov et al., 2009; McWilliams et al., 2012; Svendsen and Ahrens, 1987; see also Chapter 2.16). A possible phase transition in MgO was identified in gas-gun shock experiments at ~170 GPa (Zhang et al., 2008), but the nature of this transformation is poorly constrained. At higher pressures, laser-shock measurements of the EOS, temperature, and optical reflectivity reveal two temperature discontinuities, which are interpreted as the B1–B2 phase transformation at ~400 GPa and 9000 K and melting at ~650 GPa and 14 000 K (McWilliams et al., 2012). Based on optical reflectivity measurements, the liquid is metallic at these conditions. x-Ray diffraction measurements on ramp-compressed MgO have directly detected the B1–B2 phase transition at ~600 GPa (Coppari et al., 2013). The observed transition pressure under ramp loading is consistent with both theoretical calculations and shock wave data given the expected negative P - T

Clapeyron slope of the transition. The x-ray measurements further show that the B2 phase also remains stable to a peak pressure of 900 GPa, the highest-pressure x-ray diffraction data yet reported on any solid (Coppari et al., 2013).

The melting curve of MgO at ~Mbar pressures is controversial with a large discrepancy between experimental and theoretical determinations (Alfe, 2005; Belonoshko et al., 2010; Strachan et al., 1999; Tangney and Scandolo, 2009; Zerr and Boehler, 1994; Zhang and Fei, 2008). The recent laser-shock temperature measurements (McWilliams et al., 2012) indicate that melting occurs much higher than the P - T conditions for Hugoniot melting predicted from first-principles MD calculations (de Koker and Stixrude, 2009). A recent study of the Mg–O system using ab initio structure search methods up to 850 GPa found, in addition to MgO, that two additional compounds, MgO₂ and Mg₃O₂, become stable at 116 and 500 GPa, respectively (Zhu et al., 2013).

2.07.5.2.2 FeO

Wüstite, Fe_{1-x}O, is of importance for both the mantles and the cores of terrestrial planets. As discussed earlier, the (Mg,Fe)O solid solution is a major component of terrestrial mantles. The amount of FeO in the mantle affects the electrical and thermal conductivity of the region. FeO can also be a major alloying component of the core. Phase relations in FeO are shown in Figure 15. At lower temperatures, wüstite undergoes transformations from the B1 structure to a distorted structure and then to the B8 (NiAs-type) structure at Mbar pressures (Fei and Mao, 1994). At high temperatures, the B1 phase undergoes an insulator to metal transformation at ~70 GPa (Fischer et al., 2011; Gramsch et al., 2003; Ohta et al., 2012a). As a result, a miscibility gap would be expected to form in the (Mg,Fe)O system at

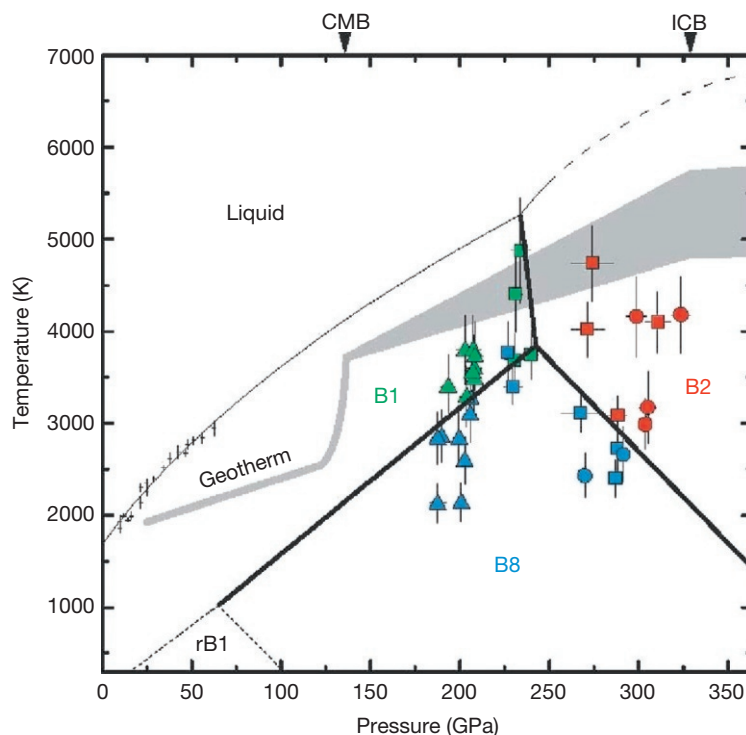


Figure 15 Phase diagram of FeO showing boundaries for B1, B2, B8, and rhombohedral phase (rB1). The melting curve and a representative geotherm for Earth are also indicated. CMB and ICB designate Earth core–mantle boundary and inner core boundary, respectively. Reproduced from Ozawa H, Takahashi F, Hirose K, Ohishi Y, and Hirao N (2011) Phase transition of FeO and stratification in Earth's outer core. *Science* 334(6057): 792–794. <http://dx.doi.org/10.1126/science.1208265>, with permission.

high pressures. The metallic behavior of FeO should also allow oxygen to dissolve more readily into metallic cores. B1 FeO eventually transforms to the B2 structure at 240 GPa (and ~ 4000 K) (Ozawa et al., 2011), compared with ~ 600 GPa for MgO (Coppari et al., 2013). The variation of the B1–B2 transition pressure for intermediate (Mg,Fe)O compositions is unknown. The melting curve of FeO has been measured to 77 GPa and 3100 K (Fischer and Campbell, 2010).

2.07.5.2.3 SiO₂

Silica is the most abundant oxide component of terrestrial mantles and serves as an archetype for the dense highly coordinated silicates of planetary interiors. While free SiO₂ is only expected in localized regions in Earth's mantle such as subducted oceanic crust, the wider range of plausible compositions and higher P – T conditions in super-Earth exoplanets allow for greater possible presence of silica phases in terrestrial exoplanets. The stability of silicate phases may be affected by polymorphism in SiO₂, and silicate disproportionation could produce silica-rich regions in deep interiors.

Over the pressure range of the Earth's crust and mantle, SiO₂ undergoes a well-known sequence of phase transitions (Figure 16). Quartz transforms first to coesite and then to octahedrally coordinated stishovite above ~ 10 GPa. At ~ 50 GPa, stishovite transforms to the orthorhombic CaCl₂-type structure (Kingma et al., 1995; Tsuchida and Yagi, 1989). SiO₂ undergoes a further transformation to the α -PbO₂-type structure at pressures near those of the Earth's core–mantle

boundary region (Karki et al., 1997b; Murakami et al., 2003). The highest-pressure transformation yet observed experimentally is to the pyrite-type structure (with 6 + 2 coordination of oxygen around Si⁴⁺) at around 270 GPa (Kuwayama et al., 2005).

Further phase transformations of SiO₂ have been explored using theoretical calculations and analog systems. DFT predictions of transformation of SiO₂ to a cotunnite-type phase around 690–750 GPa (at 0 K) have been reported (Oganov et al., 2005; Umemoto et al., 2006a). This involves a large increase in Si⁴⁺ coordination from 6 + 2 (pyrite) to ninefold coordination (cotunnite). However, more recent theoretical calculations have reported that instead, the hexagonal Fe₂P-type phase is the stable phase of SiO₂ above 700 GPa and 0 K (Tsuchiya and Tsuchiya, 2011; Wu et al., 2011). This phase has been also predicted to occur in TiO₂ and GeO₂ and has now been observed experimentally in TiO₂ (Dekura et al., 2011a,b).

Due to the change in coordination, the volume change associated with the post-pyrite transition is predicted to be large (~ 4 – 5%) (Tsuchiya and Tsuchiya, 2011). The high-temperature behavior of the new SiO₂ phases was explored using the QHA (Tsuchiya and Tsuchiya, 2011; Wu et al., 2011). The transformation to a postpyrite phase in SiO₂ is found to have a negative Clapeyron slope due to the increase in bond lengths and coordination number resulting in an increase in vibrational entropy across the transition (Wu et al., 2011). At low temperatures, SiO₂ transforms from the pyrite-type to the Fe₂P phase, whereas at higher

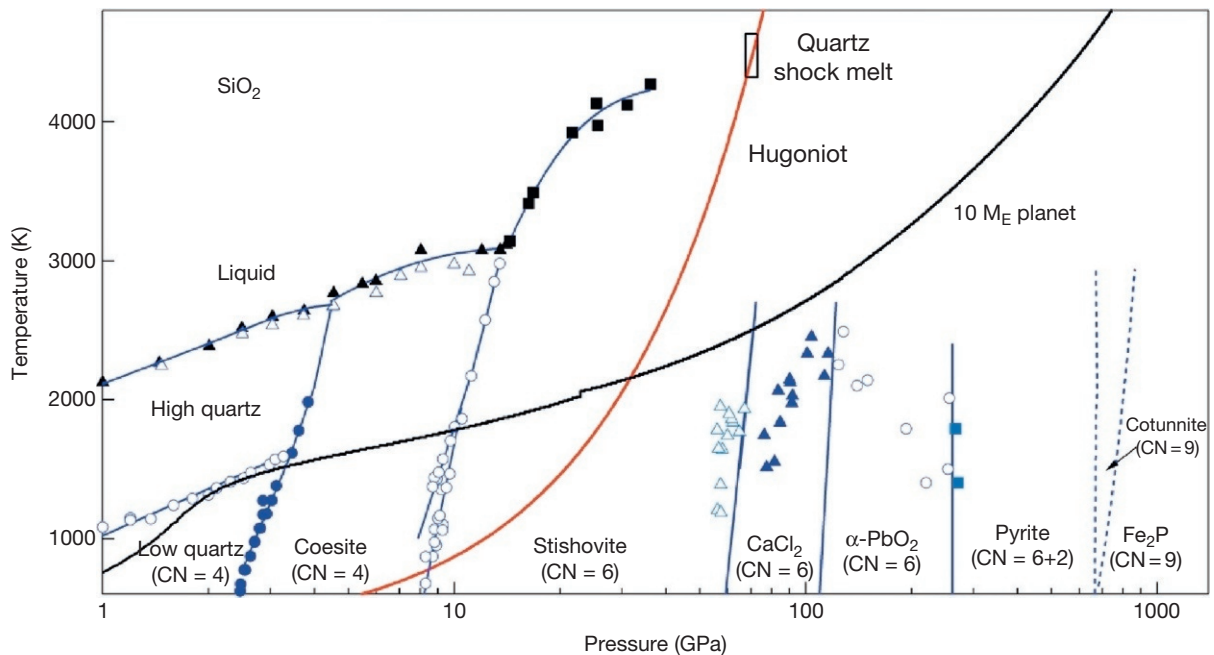


Figure 16 Phase diagram of SiO_2 showing the sequence of phase transitions up to 1000 GPa. Solid lines show experimentally determined phase boundaries, and dashed lines show theoretical boundaries for highest-pressure phases. Symbols indicate experimentally measured points along the phase boundaries. The Hugoniot curve is indicated in red with the melting point shown. A representative P - T path for a $10 M_E$ planet is shown.

temperatures, the pyrite phase first transforms to the cotunnite-type phase followed by a second transformation to the Fe_2P phase (with $<1\%$ volume change). The transformation from Fe_2P -type to cotunnite-type phase is expected to have a positive Clapeyron slope. Along the possible P - T path for a super-Earth, the pyrite-cotunnite transformation is expected to occur for planets of approximately $5 M_E$ or greater. The cotunnite- Fe_2P transformation would be expected in planets of ~ 7 or more M_E . Cotunnite-type SiO_2 at super-Earth interior conditions is predicted to have electrical conductivities close to metallic values (Umehoto et al., 2006a).

The high-pressure behavior of SiO_2 has also been explored extensively using dynamic experiments (see Chapter 2.16). Shock compression data for fused silica and quartz up to 200 GPa are interpreted as indicating transitions to stishovite and/or stishovite-like phase(s) with melting occurring above 120 GPa along the Hugoniot (Akins and Ahrens, 2002; Lyzenga et al., 1983). Measurement of the Hugoniot EOS has been extended up to 1600 GPa in recent experiments at the Sandia Z facility (Knudson and Desjarlais, 2009). Shock temperature measurements up to 1000 GPa show evidence for pronounced changes in the structure of liquid SiO_2 including dissociation and enhanced electron mobility (Hicks et al., 2006). A study of the shock vaporization of silica has recently been conducted yielding a wide ranging EOS that can be applied to better understand and potentially detect giant impacts in extrasolar planetary systems (Kraus et al., 2012).

2.07.5.2.4 MgSiO_3

MgSiO_3 in Earth's lower mantle crystallizes in the perovskite structure except for a thin layer of postperovskite near its base

(Tronnes, 2010; see also Chapter 2.03). The higher internal pressures of large terrestrial-type exoplanets mean that the postperovskite phase should play a large or even dominant role in the interiors of these bodies (Figure 17; Valencia et al., 2007a; Wagner et al., 2012). Silicate perovskite and postperovskite also to incorporate iron (see Chapter 2.03) with the distribution of Fe among phases in the lower mantle are controlled by partitioning between $(\text{Mg,Fe})\text{SiO}_3$ and $(\text{Mg,Fe})\text{O}$ (Tronnes, 2010). Iron in mantle minerals may undergo spin transitions at high pressure that may have important effects on the stability and other properties of silicate and oxide phases (Badro et al., 2004; Lin et al., 2013).

Experimental studies have demonstrated the stability of the postperovskite structure in $(\text{Mg,Fe})\text{SiO}_3$ to pressures approaching 200 GPa, although some evidence for modifications of the structure has been reported (Yamanaka et al., 2012). Germanates are known to be good analogs for silicates, with similar sequences of phase transitions occurring at lower pressures due to the larger ionic radius of Ge^{4+} compared with Si^{4+} . The phase stability and EOS of MgGeO_3 have been studied to 200 GPa in the DAC, and the postperovskite phase remains stable until at least this pressure (Kubo et al., 2006). Fluorides including NaMgF_3 , NaNiF_3 , and NaCoF_3 are also expected to be good analogs for MgSiO_3 due to their close similarity in structural properties (Dobson et al., 2011; Duffy, 2008). High-pressure experiments and theoretical calculations on NaMgF_3 yield conflicting results with one experimental study reporting evidence for transformation to an unknown NaMgF_3 structure above 30 GPa (Martin et al., 2006) and another reporting the stability of NaMgF_3 postperovskite to at least 70 GPa and 2500 K (Grocholski et al., 2010). These contrast with

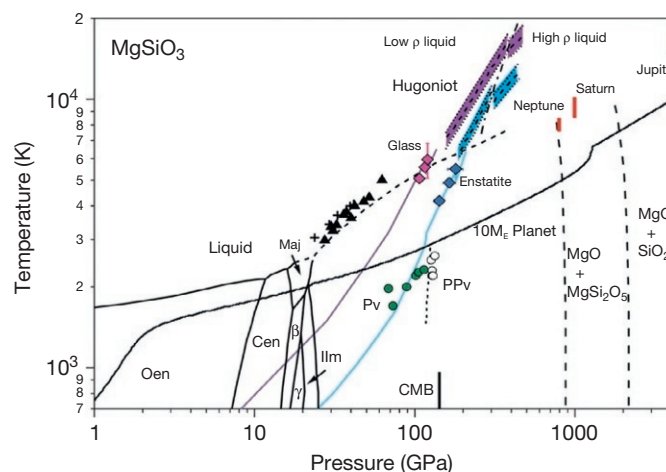


Figure 17 Phase diagram of MgSiO_3 showing sequence of phase transitions up to 2000 GPa. Blue and purple curves show shock Hugoniot for MgSiO_3 crystals (enstatite) and glass, respectively, with blue and purple diamonds showing representative gas-gun data. The black dashed lines with blue- and purple-shaded regions show laser-shock data indicating the presence of density discontinuity in the liquid regime. Experimental data are also shown for the melting curve (black symbols) and Pv-PPv boundary (green and open circles). Estimated P - T conditions for a $10 M_E$ super-Earth and cores of Jupiter, Saturn, and Neptune are indicated. Oen, orthoenstatite; Cen, clinoenstatite; β , wadsleyite + SiO_2 ; γ , ringwoodite + SiO_2 ; ilm, ilmenite; Maj, majorite; Pv, perovskite; PPv, postperovskite; CMB, Earth's core-mantle boundary.

theoretical calculations that predict the disproportionation of NaMgF_3 postperovskite into NaF and MgF_2 above about 40 GPa (Umemoto et al., 2006b).

Shock compression studies of MgSiO_3 have extended to as high as 950 GPa (Mosenfelder et al., 2009; Spaulding et al., 2012; see also Chapter 2.16). Laser-shock experiments have reported evidence for a liquid-liquid phase transition in MgSiO_3 melt at 300–400 GPa and 10000–16000 K with a large volume change of $\sim 6\%$ (Spaulding et al., 2012; Figure 17). A recent theoretical study has suggested that this transition may instead represent decomposition into solid MgO and liquid SiO_2 (Boates and Bonev, 2013). Measurements of optical reflectivity suggest that the melt is metallic at temperatures above ~ 12000 K (Spaulding et al., 2012).

Initial theoretical calculations examining the stability of MgSiO_3 perovskite to ultrahigh pressures predicted that MgSiO_3 postperovskite breaks down into an oxide mixture of MgO (B2 phase) and SiO_2 (cotunnite-type phase) at ~ 1100 GPa (Umemoto et al., 2006a). However, this work did not consider the more recently discovered hexagonal Fe_2P phase of SiO_2 or possible dissociation of ABO_3 compounds into AO and AB_2O_5 (Okada et al., 2011; Wu et al., 2009) or AO and AB_3O_7 (Nishio-Hamane et al., 2012). More recent theoretical calculations predict that MgSiO_3 pPv will dissociate into CsCl-type MgO and MgSi_2O_5 ($\text{P2}_1/\text{c}$ -type) at 900 GPa (Umemoto and Wentzcovitch, 2011; Figures 13 and 17). The volume change associated with this transition is $\sim 2\%$, and the Si^{4+} coordination increases from 6 in postperovskite to 7–8 in MgSi_2O_5 . A further dissociation of MgSi_2O_5 into MgO and SiO_2 (Fe_2P phase, ninefold coordination) is also predicted to occur with a small volume change at 2.1 TPa, a pressure above the maximum expected to occur in super-Earth mantles (Umemoto and Wentzcovitch, 2011). Quasiharmonic calculations suggest both dissociation reactions are endothermic with negative Clapeyron slopes, thereby yielding a wider stability

field for the dissociation products at higher temperatures. The negative Clapeyron slope arises due to changes in the vibrational density of states resulting from increasing Si–O bond lengths as Si^{4+} coordination increases across each transition.

2.07.5.2.5 CaSiO_3 and CaO

CaSiO_3 perovskite is the third most abundant phase in Earth's mantle. Theoretical calculations find that at 0 K, CaSiO_3 perovskite transforms to postperovskite above 500 GPa and then dissociates to CaO (B2 phase) and SiO_2 (Fe_2P phase) around 700 GPa (Tsuchiya and Tsuchiya, 2011). However, at the higher temperatures expected in exoplanets, quasiharmonic calculations indicate that the postperovskite phase is not stable and CaSiO_3 perovskite directly decomposes to CaO (B2) and SiO_2 (pyrite type) at 600 GPa (Tsuchiya and Tsuchiya, 2011; Figure 13). The breakdown of CaSiO_3 occurs at considerably lower pressure than the stability limit of MgSiO_3 (~ 900 GPa). SiO_2 liberated by the breakdown of CaSiO_3 would react with MgO to increase the total abundance of the postperovskite phase (Tsuchiya and Tsuchiya, 2011). The oxide CaO transforms to the B2 phase at low pressures of ~ 60 GPa (Jeanloz et al., 1979; Mehl et al., 1988; Figure 13). The B2 phase of CaO is predicted theoretically to metallize at ~ 400 GPa, but other oxides (SiO_2 and MgO) remain insulating to 2000 GPa at low temperatures (Oganov et al., 2003; Tsuchiya and Tsuchiya, 2011).

2.07.5.2.6 Al_2O_3

Al_2O_3 crystallizes in the corundum structure at ambient conditions and undergoes transformations to the Rh_2O_3 -II structure at ~ 90 GPa and the CaIrO_3 structure at ~ 130 GPa (Cynn et al., 1990; Funamori and Jeanloz, 1997; Marton and Cohen, 1994; Oganov and Ono, 2005; Figure 13). Metallization of Al_2O_3 may occur at pressures of ~ 300 GPa (Nellis, 2010). DFT calculations predict further structural transformation at

370 GPa to a U_2S_3 -type phase (Umemoto and Wentzcovitch, 2008). For the Earth, the Al_2O_3 component of the mantle is largely dissolved into the $(\text{Mg,Fe})\text{SiO}_3$ perovskite, post-perovskite, or other Al-rich phases and free Al_2O_3 is not expected. The change in cation coordination from six to seven in the U_2S_3 phase may favor exsolution of Al_2O_3 out of the postperovskite phase in deep super-Earths with possible resulting changes in electrical and thermal conductivities for the assemblage (Umemoto and Wentzcovitch, 2008).

2.07.5.2.7 Iron and iron alloys

Under pressure, iron transforms from the body-centered-cubic (bcc, α) phase to a hexagonal-close-packed (hcp, ϵ) phase near 13 GPa. Most experiments suggest that the hcp phase remains stable to higher pressures up to those of Earth's core (Kuwayama et al., 2008; Ma et al., 2004; Shen et al., 1998; Tateno et al., 2010), although some experimental evidence for new phases has been reported (Andrault et al., 1997; Dubrovinsky et al., 2000). Theoretical calculations report conflicting results with some studies favoring the stability of hcp iron at Earth core conditions (Modak et al., 2007; Vočadlo et al., 1999), while various other possible phases have been also proposed including bcc (Belonoshko et al., 2011; Bouchet et al., 2013; Luo et al., 2010), face-centered-cubic (fcc) (Mikhaylushkin et al., 2009), or stacking disordered phases (Cottenier et al., 2011; Ishikawa et al., 2011). Recently, static DAC experiments have reached inner core conditions up to 377 GPa and 5700 K (Tateno et al., 2010) and found that the hcp phase of Fe is stable. However, further studies at these extreme conditions are needed for confirmation.

The EOS of iron has been studied under quasihydrostatic conditions in the DAC up to 300 GPa (Dewaele et al., 2006; Dubrovinsky et al., 2000). Extensive shock compression data sets have been obtained on iron, and a careful analysis of data to 442 GPa has been reported (Brown et al., 2000). Under shock loading, iron is observed to melt along the Hugoniot at about 230 GPa (Brown and McQueen, 1986; Nguyen and Holmes, 2004). Laser-based ramp compression experiments have constrained the quasi-isentropic compression curve of solid iron to 273 GPa (Wang et al., 2013).

Theoretical DFT studies have examined the stable phases and structure of iron to pressures as high as 100 TPa (Cottenier et al., 2011; Pickard and Needs, 2009; Stixrude, 2012). The hcp phase is found to be stable at 0 K to pressures of and well beyond those of Earth's core. A transformation to an fcc phase occurs at 6–7 TPa with a volume change of $\sim 0.15\%$. At even higher pressures, a body-centered-tetragonal phase is stabilized at 34–38 TPa. Ab initio random structure searching showed that only these high-symmetry close-packed phases are energetically competitive candidates for iron (Pickard and Needs, 2009). Results at finite temperatures on these close-packed phases have been reported using the QHA and are consistent with the 0 K results (Stixrude, 2012; Figure 18). The central pressure for a large ($10 M_E$) super-Earth is expected to be around 4 TPa (Wagner et al., 2012) and that of Jupiter ($\sim 300 M_E$) is around 7 TPa. Thus, hcp iron is likely the stable phase under conditions of all or nearly all super-Earths, but the high-pressure phases of iron would be expected to exist in the cores of super-Jupiters. However, other recent theoretical studies suggest that bcc iron or more complex structures composed

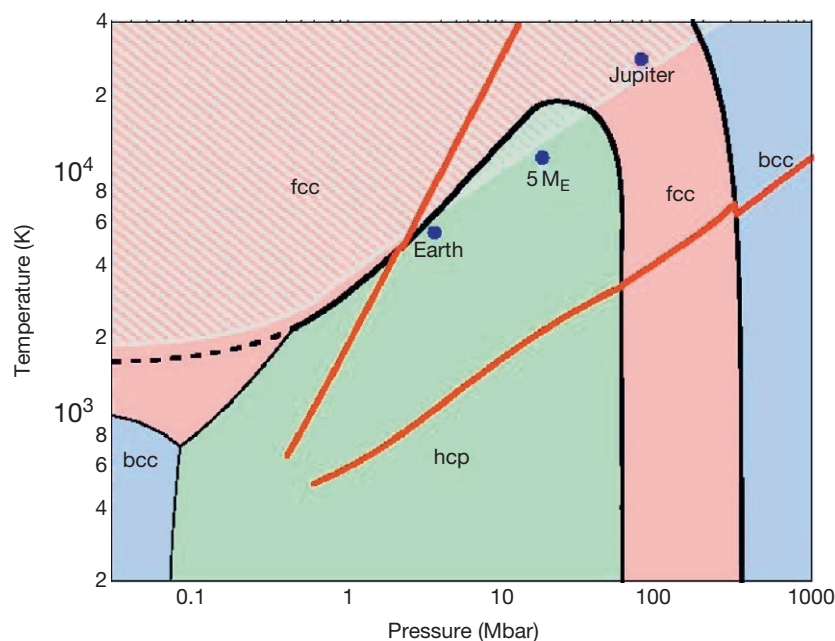


Figure 18 Phase diagram of Fe at ultrahigh pressures. Thin black lines show experimental phase boundaries; thick black lines are from theoretical calculations. The red lines show calculated isentropes (lower) and Hugoniot curves (upper). P - T conditions at the center of the Earth, a super-Earth with mass five times the Earth's mass, and Jupiter are shown by the blue circles. The stability field of liquid iron, indicated by the hatching, is estimated from computed vibrational frequencies and Lindemann's law. bcc, body-centered-cubic phase; fcc, face-centered-cubic phase; hcp, hexagonal-close-packed phase. Reproduced from Stixrude L (2012) Structure of iron to 1 Gbar and 40 000 K. *Physical Review Letters* 108(5): 055505. <http://dx.doi.org/10.1103/PhysRevLett.108.055505>, with permission.

of periodic stacking fault sequences are candidate structures for exoplanet cores (Bouchet et al., 2013; Cottenier et al., 2011). The stable phase of iron may also be affected by impurity content (Dubrovinsky et al., 2007). There have been extensive experimental and theoretical studies of various iron alloys that are candidate Earth core components (Chapter 2.06), but few constraints exist as yet at P - T conditions relevant to super-Earths.

Using ab initio MD simulations, the melting curve of iron has been computed to pressures up to 1500 GPa (Bouchet et al., 2013; Morard et al., 2011). The results are in good agreement with earlier calculations extending up to pressures of the Earth's inner core. By comparing to P - T conditions expected in super-Earths from interior models (Sotin et al., 2007; Valencia et al., 2006; Wagner et al., 2012), it was found that Clapeyron slope of the melting curve exceeded the geotherm for super-Earths and the likelihood of a molten core decreases as the size of a terrestrial planet increases (Morard et al., 2011). Recent thermal evolution models suggest that an inner core will not develop for super-Earths greater than $2.5 M_E$ (Gaidos et al., 2010). However, the role of melting point depression of iron due to alloying components remains to be evaluated. There is also a need for more studies on the key physical properties of iron and iron alloys necessary for understanding core energetics and dynamics for super-Earths. A number of thermodynamic properties (thermal expansivity, Grüneisen parameter, etc.) of iron have been evaluated up to 1500 GPa and high T using ab initio MD computations (Bouchet et al., 2013).

2.07.5.2.8 Diamond and carbides

Carbon-rich planets may result from C enrichment of a local area of the protoplanetary disk or due to variation in host star chemical abundance (Bond et al., 2010). Carbon is the fourth most abundant element in the cosmos and a key constituent of many planets. Ice giants such as Neptune and Uranus contain large quantities of methane (Hubbard et al., 1991) that decomposes under high-pressure and high-temperature conditions, possibly forming diamond-rich layers in the interior (Ancilotto et al., 1997; Benedetti et al., 1999; Ross, 1981). Static DAC experiments have constrained the EOS of diamond to 140 GPa (Occelli et al., 2003), while maximum static pressures of up to 400 GPa have been reached on diamond samples (Akahama and Kawamura, 2010; Wang et al., 2010). Using laser-based ramp compression, the pressure-density relationship and strength of diamond have been characterized up to 800 GPa (Bradley et al., 2009).

Theoretical calculations predict that diamond will transform to the BC8 structure at around 1 TPa followed by a further transition to a simple-cubic structure near 3 TPa (Correa et al., 2008; Grumbach and Martin, 1996; Yin, 1984; Yin and Cohen, 1983; Figure 19). The BC8 phase remains tetrahedrally coordinated and strongly covalently bonded but is about 10% denser than diamond due to denser packing of tetrahedra. It is also predicted to be weakly metallic. The transition to the simple-cubic structure results in an increase in coordination number to six. Experimental evidence for the existence of a new solid phase, possibly BC8, in shock-compressed diamond, has been reported at around 850–900 GPa (Knudson et al., 2008). Ab initio random structure search methods have been used to

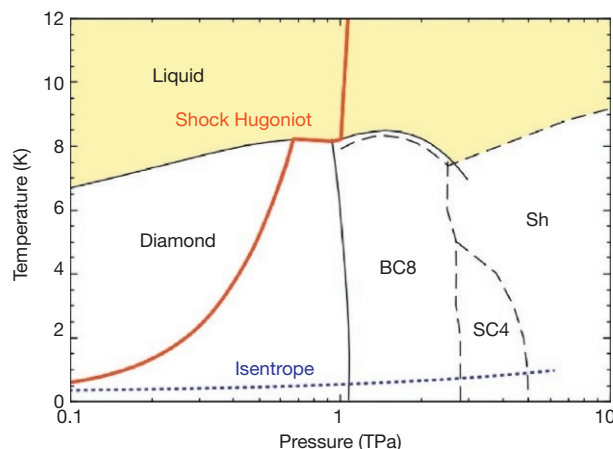


Figure 19 Phase diagram of carbon at ultrahigh pressures. Isentrope is shown as blue dotted line, and shock Hugoniot is solid red line. The yellow region is liquid carbon. SC4, simple-cubic phase; Sh, simple-hexagonal phase. Reproduced from Rygg JR, et al. (2012) Powder diffraction from solids in the terapascal regime. *Review of Scientific Instruments* 83(11): 113904. <http://dx.doi.org/10.1063/1.4766464>, with permission.

predict a further sequence of transformations from simple-cubic, to simple-hexagonal (6.4 TPa), to fcc (21 TPa), to double hcp (270 TPa), to bcc (650 TPa) phase (Martinez-Canales et al., 2012). The fcc phase of carbon has the interesting property that it is an electride in which electrons play the role of anions in the structure.

The melting behavior of diamond has also attracted much interest (Figure 19). Theoretical studies have predicted a maximum in the melting curve around 500 GPa and 8000–9000 K (Correa et al., 2006; Grumbach and Martin, 1996; Wang et al., 2005; Wu et al., 2002). Also, a triple point between diamond, the BC8 phase, and liquid is predicted to exist at ~850 GPa from ab initio MD simulations (Correa et al., 2006). Shock compression experiments on diamond have been carried out to as high as 4 TPa (Bradley et al., 2004; Brygoo et al., 2007; Eggert et al., 2009; Hicks et al., 2008; Knudson et al., 2008; Nagao et al., 2006). These studies reveal that at 600–1100 GPa, diamond melts to a dense metallic fluid with a negative melting slope consistent with the theoretical predictions.

SiC is a potential major phase in carbon-rich planets. Its behavior has been explored under both static and shock compressions to as high as 160 GPa. At ~100 GPa, SiC undergoes a transition from the wurtzite to rock-salt structure with a large (~15%) density increase (Sekine and Kobayashi, 1997; Yoshida et al., 1993). Due to such a large density change, this transformation could be a major structural feature in carbide-rich exoplanets. EOS data for the high-pressure phase of SiC are not available, and so models to date have used EOS parameters for the low-pressure phase (Madhusudhan et al., 2012; Seager et al., 2007). The thermal structure of a carbide-rich planet may be drastically different from planets with silicate/oxide-dominated mantles due to large variations in physical properties. For example, the thermal conductivity of SiC is two orders of magnitude greater than that of silicates and oxides, likely implying major differences in thermal structure and evolution (Madhusudhan et al., 2012). Additionally, SiC has been found

to have a negative Clapeyron slope for melting, at least up to modest pressures (~ 8 GPa) (Sokolov et al., 2012), and may result in a solid SiC layer underlain by a molten SiC layer, provided that the densities remain high for the melt.

2.07.5.2.9 H_2O

In addition to planets with largely dry and rocky compositions, super-Earths may also encompass a significant amount of water along with refractory components (ocean planets) (Léger et al., 2004) or may be dominantly composed of ices with a H_2 -He envelope (sub-Neptunes). Such planets might form outside the snow line of the protoplanetary disk allowing them to accrete and retain significant quantities of ice and, in some circumstances, could subsequently migrate inward. The ability to retain H_2 -He and H_2O over the planet's evolution will depend on a number of factors including its final distance from the host star. H_2O ice is a complex material with 16 stable or metastable crystalline phases identified experimentally (Figure 20). At temperatures above 150 K, ice VI occurs approximately from 0.6 GPa until it transforms to ice VII at 2.2 GPa. Ice VII is stable to ~ 70 GPa where it transforms to ice X. In this phase, the structure adopts a symmetric configuration in which oxygen atoms form a bcc lattice and the hydrogen atoms are located at the midpoints between two nearest-neighbor oxygen atoms. A further transformation from ice X to a new phase (ice XI) is predicted to occur at ~ 3 Mbar and to remain stable up to at least ~ 2000 K and 4 Mbar, based on ab initio MD simulations (Benoit et al., 1996). Higher-pressure phase transitions have been explored using DFT-

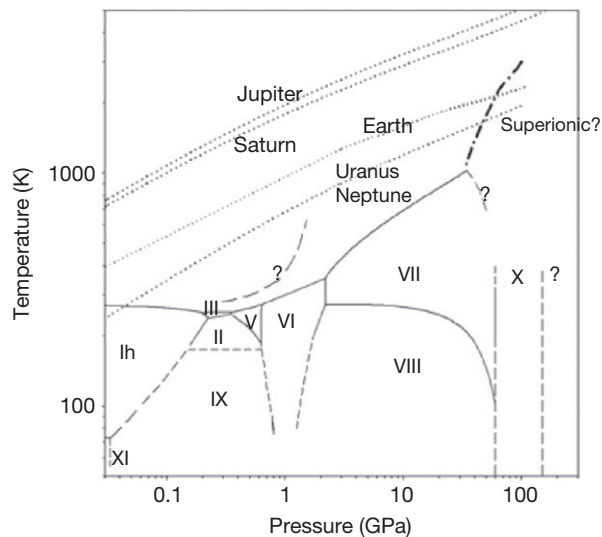


Figure 20 High-pressure-temperature phase diagram of H_2O . The Roman numerals are various phases of solid ices. Ih represents ice in the hexagonal crystal structure stable at ambient conditions. Black solid lines show experimentally determined phase boundaries; dashed lines show schematic phase boundaries; dotted lines show isentropes of Jupiter, Saturn, Uranus, and Neptune, respectively, and geotherm of the Earth. The dashed line in the liquid region is a proposed liquid-liquid transition. Reproduced from Lin et al. (2005) *Melting behavior of H_2O at high pressures and temperatures*. *Geophysical Research Letters* 32: L11306, with permission.

based structure searching methods (Hermann et al., 2012; Ji et al., 2011; Militzer and Wilson, 2010).

Assuming full differentiation, a rocky planet with a substantial H_2O /ice component would feature H_2O layer(s) overlying the rocky mantle and metallic core. Depending on surface P - T conditions, H_2O at the surface of such a planet could be solid or liquid, possibly forming a liquid ocean to depths of ~ 100 km (Léger et al., 2004). Because the slope of adiabatic temperature gradient in the liquid H_2O layer is lower than the slope of the melting curve of high-pressure ice phases, the water layer would eventually freeze into ice VI or ice VII. Ice VII eventually transforms at ~ 70 GPa to ice X, which is stable to at least 150 GPa. For a planet that is 50 wt% H_2O , the P - T conditions at the base of the ice layer are estimated to be ~ 50 GPa and < 1000 K (Sotin et al., 2007) for a $1 M_E$ planet. The thickness of the ice layer would range from 3000 to 6000 km for planets ranging from 1 to $10 M_E$ (Sotin et al., 2007).

2.07.6 Physical Properties of Minerals at Super-Earth Conditions

Mineralogical phase transitions change the density structure of a planet, although the effect on the mass-radius relationship is not expected to be large in many cases (Swift et al., 2012). Changes in crystal structure, however, can affect other key properties including melting temperature, thermal expansivity, Grüneisen parameter, thermal and electrical conductivities, and rheological properties, which are all critical for understanding the structure, dynamics, and evolution of exoplanets. Because of the wider range of pressures and temperatures encountered in super-Earth interiors, the depth dependence of thermodynamic, rheological, and transport properties may become especially important.

2.07.6.1 Rheology

The thermal structure, convective regime, tectonic and magmatic activity, propensity for plate tectonics, and existence of a magnetic field are all properties strongly influenced by the viscosity structure of a planet. The viscosity is determined by the rheological properties of the constituent minerals. Under the high-temperature, low-stress conditions expected in terrestrial planetary mantles, viscous deformation of solids is controlled by thermally activated motion of crystalline defects (Karato, 2008; Poirier, 1985). The pressure and temperature dependence of the viscosity, η , can be described in a simplified Arrhenius-type formulation (Karato, 2011; Wagner et al., 2012):

$$\eta(P, T) = b \exp\left(\frac{E^* + PV^*(P)}{RT}\right) \quad [17]$$

where b is a constant, R is the gas constant, E^* is the activation energy, and V^* is the activation volume. Viscosity is both strongly pressure- and temperature-dependent with the activation energy controlling the temperature effect of viscosity and the activation volume controlling the pressure effect.

In the Earth, viscosity increases with pressure due to reduction of the activation volume for creep. The viscosity of the deep lower mantle is estimated to be 10–100 times

higher than Earth's upper mantle (see [Chapter 7.02](#)). However, direct experimental measurements of the effect of pressure on activation volume are limited and uncertain. One approach to estimate the effect of pressure on viscosity for conditions relevant to a $10 M_E$ planet is by scaling with the homologous temperature, T/T_m , where T_m is the melting temperature ([Stamenkovic et al., 2011](#)). The melting temperature of perovskite, taken to be representative of exoplanet mineralogy, was inferred from Lindemann's law, which assumes that melting occurs when the root-mean-square atomic displacements reach a critical fraction of the interatomic spacing. Using this approach, the mantle viscosity was predicted to increase greatly by up to 15 orders of magnitude across the adiabatic mantle of a $10 M_E$ planet ([Stamenkovic et al., 2011](#)). The viscosity at the bottom of the mantle in this case would be sufficiently large that a conductive lid would form above the core-mantle boundary with major effects on the thermal structure and evolution of the planet ([Stamenkovic et al., 2012](#)).

Vacancy diffusion rates in $MgSiO_3$ perovskite and post-perovskite at lower mantle conditions have been calculated using first-principles methods and transition state theory ([Ammann et al., 2010](#)). The predicted viscosity of the two phases inferred from the diffusion-controlled creep strength is different with viscosities in postperovskite up to four orders of magnitude lower than perovskite. Postperovskite also exhibits highly anisotropic behavior with several orders of magnitude difference in activation energy in different directions. These results for postperovskite have subsequently been extended to pressures up to 1 TPa, leading to a prediction of viscosities ($\sim 10^{25}$ – 10^{26} Pa s) in the deep mantle of a large super-Earth (7–10 M_E). These are only 4–5 orders of magnitude greater than those in the Earth's lower mantle. Corresponding numerical convection calculations find that convection can still occur in the deep mantle of such a planet due to feedbacks between internal heating, temperature, and viscosity ([Tackley et al., 2013](#)). However, it has also been argued that the theoretical calculations on defect mobility in postperovskite are not sufficient to constrain creep behavior of this mineral ([Karato, 2010](#)).

Other recent work, on the other hand, suggests that the solid viscosity in large exoplanet mantles may be relatively low at depth ([Karato, 2011](#)). Pressure weakening is predicted to occur due to several factors. One is the expected change in the mechanism of diffusion from vacancy to interstitial-dominated beginning at ~ 100 GPa. In general, oxides are weaker than silicates and B2 oxides are weaker than B1 oxides ([Karato, 1989](#)). As such, dissociation of $CaSiO_3$ and $MgSiO_3$ forming B2-type MgO and CaO at 600–1100 GPa will increase the volume fraction of these relatively weak oxides. If metallization of the oxides occurs at high P – T , it may lead to further weakening. As a result of these factors, the deep mantle viscosity of terrestrial super-Earths may decrease as planetary mass increases. The deep mantle of a large rocky super-Earth may have viscosities that are 100–1000 times lower than those of Earth's lower mantle ([Karato, 2011](#)). Whether MgO and CaO would be sufficiently abundant to control the rheological properties of the mixture will ultimately depend on the bulk composition of the planet's mantle and whether complete ([Umemoto et al., 2006a](#)) or partial dissociation ([Umemoto](#)

and [Wentzcovitch, 2011](#)) of $MgSiO_3$ occurs. Clearly, in view of the large differences of the previously mentioned studies, there remains substantial uncertainty about the rheological behavior at these extreme conditions, as there are many orders of magnitude differences in viscosity estimates in super-Earth interiors.

In addition to their potential effect on rheology, phase transitions can promote layered convection when accompanied by a strong negative Clapeyron slope that resists convection ([Tackley et al., 1993](#); [van den Berg et al., 2010](#)). Temperatures in super-Earth interiors are highly uncertain as discussed in previous sections. The temperature has a strong effect on rheology, and there is a feedback between temperature and rheology that regulates the heat loss of a planet and influences its thermal evolution. The proximity of many candidate super-Earths to their host star means that they are expected to be in synchronous rotation and subjected to strong tidal forces. The amount and distribution of tidal heating will depend on the viscosity, shear modulus, and density ([Moore, 2003](#)). Tidal friction can contribute substantially to the total heat budget of short-period super-Earths ([Henning et al., 2009](#)). Orbital evolution of exoplanets is also an important phenomenon. Lower viscosities would favor higher tidal heating rates and therefore faster orbital evolution.

2.07.6.2 Thermal Expansivity and Thermal Conductivity

Thermal expansivity, α , determines the buoyancy in the deep mantle and hence influences convective motion in planets. Thermodynamic calculations for mantle phases yield estimates of approximately an order of magnitude decrease in thermal expansivity from ambient pressure up to ~ 1 TPa along a plausible super-Earth temperature profile ([Stamenkovic et al., 2011](#); [Wagner et al., 2012](#)). This is much greater than the ~ 2.5 times decrease in α expected across the Earth's mantle, and this strong decrease may affect the style and vigor of convection in super-Earth deep mantles. There are as yet few experimental measurements or theoretical calculations of thermal expansivity in the multimegabar range relevant to super-Earth interiors.

Thermal conductivities of mantle phases are also important parameters for thermal models. The thermal conductivity controls the temperature gradient across boundary layers that transfer heat conductively. However, this property is not well constrained for mantle minerals due to difficulties in both theoretical calculations and experiments at high pressures and temperatures. Thermal conductivity is the sum of a phonon or lattice component, a radiative component, and an electronic component. The phonon contribution is expected to be dominant under high-pressure interior conditions. In general, the phonon contribution to thermal conductivity increases with pressure, and this would tend to reduce convective vigor as planetary size increases ([Wagner et al., 2012](#)). At the high temperatures of exoplanet interiors, the electronic component of thermal conductivity may play an increasingly strong role ([van den Berg et al., 2010](#)). Experimental studies suggest that the thermal conductivity and diffusivity of postperovskite may be significantly larger than that of perovskite ([Hunt et al., 2012](#); [Ohta et al., 2012b](#)). Dissociation of silicates into oxides could affect deep mantle thermal

conductivities with expected higher conductivity in oxides (de Koker, 2010). For the largest super-Earths, metallization of mantle phases (discussed in the succeeding text) would also enhance electronic conductivities while suppressing radiative conductivity (Umemoto et al., 2006a). The potential effects of such factors on heat transport and convective dynamics in super-Earths have been explored in a number of recent works (Stamenkovic et al., 2011; Tosi et al., 2010; van den Berg et al., 2010; Wagner et al., 2012).

2.07.6.3 Electrical Conductivity and Metallization

Pressure reduces interatomic distances causing electron wave functions of neighboring ions to increasingly overlap. Eventually, outer electrons become delocalized resulting in increased electrical conductivity and ultimately metallization. Experimental and theoretical evidence for high-pressure metallization of potential super-Earth mantle phases such as FeO, MgO, Al₂O₃, SiO₂, and CaO was discussed earlier. Metallization may affect rheology and thermal and radiative heat transport. Additionally, electrically conducting phases in the deep lower mantle could potentially interact with the magnetic field generated by a core dynamo affecting possible direct or indirect observations of super-Earth magnetic fields such as by radio emission, x-ray emission from planet-hosting stars, or exoplanet atmospheric effects. Numerical dynamo models examining how metallized silicates in the deep mantles may affect the observable magnetic fields of super-Earths indicate that such metallization would reduce the detectability of dynamo-generated magnetic fields (Vilim et al., 2013). The presence of deep magma oceans in terrestrial exoplanets could lead to metallic silicate/oxide liquid regions or layers that could contribute to dynamo processes in a planet (McWilliams et al., 2012; Nellis, 2012).

2.07.6.4 Melts and Liquids

An understanding of melting behavior and the properties of liquid silicates and metal alloys at ultrahigh *P-T* conditions are also needed for super-Earth applications. Heating during accretion and differentiation in the early stages of planetary evolution is likely sufficient to melt the silicate mantle of terrestrial planets, creating magma oceans that could span a wide range of depths. Degassing of such oceans may play a major role in the development of early atmospheres and affect volatile retention in the interior. Extreme temperatures in close-in tidally locked planets with permanent day- and nightsides could result in localized lava oceans beneath the substellar point or allow enhanced magma production in the substellar hemisphere of the planet (Gelman et al., 2011; Léger et al., 2011). High internal temperatures leading to partial melting may also occur as a result of compositional layering, rheological properties, or tidal forcing. In such cases, a deep magma ocean such as proposed for Earth (Labrosse et al., 2007) may develop in terrestrial exoplanets (Tackley et al., 2013; Valencia et al., 2007b). While some constraints on melting curves and liquid properties from theory and experiment are available for some of the materials as discussed earlier, there is still considerable uncertainty in many fundamental properties including solidus temperature, melt–solid density contrast, and partitioning behavior at the pressures of 100–1000 GPa and beyond.

2.07.7 Summary and Outlook

Less than two decades after the discovery of the first confirmed extrasolar planet, there are at the time of this writing more than 900 confirmed and over 3000 additional candidate exoplanets. As techniques for detecting and probing exoplanets extend to smaller bodies more distant from their host stars, there is growing interest in understanding the prevalence and characteristics of the emerging population of super-Earth planets. Such bodies may encompass a diverse range of composition and behavior for which there may be in many cases no analog in our own solar system. Speculations about planetary types that exist include Earth-like compositions, super-Mercuries, coreless planets, core-only planets, water worlds, carbon-rich planets, and sub-Neptunes.

Inferring the mineralogy and internal structure of exoplanets is very challenging given the limited observational constraints possible, but these properties are of key importance for understanding the diversity of planetary worlds. For solid exoplanets, the interior structure is intrinsically interlinked to interpretation of observations and to models of planet formation and atmospheric processes. The interior structure not only controls the thermal evolution of the interior but also exerts a strong influence on the surface environment including the nature of the atmosphere, existence of a magnetic field, and tectonic style. The interior behavior is thus a critical ingredient for determining whether surface conditions are conducive to habitability. Ultimately, the large-scale interior processes of planets are controlled by the physical properties of the mineral constituents, which in turn are controlled by their underlying chemistry and crystal structure. Unraveling the range of structures and chemistries for the range of plausible constituents of super-Earths represents an exciting challenge for mineralogy and mineral physics in the coming years. Addressing this problem will require development of new experimental techniques to reach even higher pressures and temperatures concurrent with further advances in first-principles theoretical methods. The field of exoplanet mineralogy is in its infancy, but results to date are already leading to novel findings and substantial revisions in our understanding of how solid materials behave at extreme conditions. This chapter represents a snapshot in our understanding at this early juncture. The rapid pace of development in observation, experiment, and interpretation promises many new and exciting discoveries in the coming years.

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2.08 Thermodynamics, Phase Transitions, Equations of State, and Elasticity of Minerals at High Pressures and Temperatures

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2.08.1 Thermodynamics of Crystals

Thermodynamics provides the general basis for the theory of structure and properties of matter. This chapter gives only as much thermodynamics as needed for good comprehension of geophysics and on a relatively advanced level. For further reading, we refer to [Landau and Lifshitz \(1980\)](#), [Chandler \(1987\)](#), [Wallace \(1998\)](#), and [Bowley and Sánchez \(1999\)](#).

2.08.1.1 Thermodynamic Potentials

If one considers some system (e.g., a crystal structure) at temperature $T=0$ K and pressure $P=0$, the equilibrium state of that system corresponds to the minimum of the internal energy E :

$$E \rightarrow \min \quad [1]$$

that is, any changes (e.g., atomic displacements) would result in an increase of energy. The internal energy itself is a sum of

the potential and kinetic energies of all the particles (nuclei and electrons) in the system.

The principle [1] is valid in only two situations: (1) at $T=0$ K and $P=0$ and (2) at constant V (volume) and S (entropy), that is, if we impose constraints of constant S , V , the system will adopt the lowest-energy state. Principle [1] is a special case of a more general principle that the thermodynamic potential W describing the system be minimum at equilibrium:

$$W \rightarrow \min \quad [2]$$

As already mentioned, at constant V , S , $W_{V,S}=E \rightarrow \min$. At constant P , S , the appropriate thermodynamic potential is the enthalpy H :

$$W_{P,S}=H=E+PV \rightarrow \min \quad [3]$$

At constant V , T , the Helmholtz free energy F is the thermodynamic potential:

$$W_{V,T}=F=E-TS \rightarrow \min \quad [4]$$

At constant P , T (the most frequent practical situation), the relevant thermodynamic potential is the Gibbs free energy G :

$$W_{P,T}=G=E+PV-TS \rightarrow \min \quad [5]$$

The minimum condition implies that

$$\frac{\partial W}{\partial x_i} = 0 \quad [6]$$

However, this condition is also satisfied for maxima of the thermodynamic potential and for saddle points (Figure 1). To exclude saddle points and maxima, one has to make sure that the matrix of second derivatives of W with respect to all the degrees of freedom (in case of a crystal structure, with respect to atomic coordinates and lattice parameters)

$$H_{ij} = \frac{\partial^2 W}{\partial x_i \partial x_j} \quad [7]$$

be positive definite:

$$\det H_{ij} > 0 \quad [8]$$

Still, there may be a large (or infinite) number of minima. The equilibrium state corresponds to the lowest minimum of W

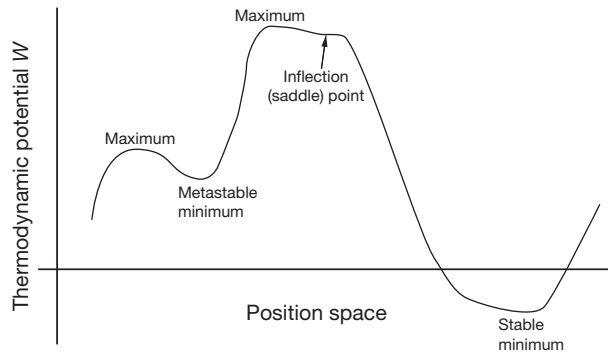


Figure 1 Extrema and saddle points in a one-dimensional representation of the (free) energy surface.

(the global minimum), whereas all the other minima are called local and correspond to metastable states. Local minima have the property of stability to an infinitesimal displacement (after any such displacement, the system returns to the initial state), but one can always find a sufficiently large energy fluctuation that will irreversibly destroy the metastable state.

2.08.1.2 Differential Relations

From the first law of thermodynamics, one has

$$dE = -PdV + TdS \quad [9]$$

Applying Legendre transformations, the following relations can be obtained:

$$dH = VdP + TdS \quad [10]$$

$$dF = -PdV - SdT \quad [11]$$

$$dG = VdP - SdT \quad [12]$$

When there is thermodynamic equilibrium between two phases (denoted 1 and 2) at given P and T , $G_1=G_2$. Moving along the two-phase equilibrium line in P - T space requires $dG_1=dG_2$, that is,

$$\Delta V dP - \Delta S dT = 0 \quad [13]$$

or, in a different form,

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} \quad [14]$$

This is the famous Clausius–Clapeyron equation.

Using eqns [9]–[12], one can express various thermodynamic parameters:

$$P = -\left(\frac{\partial E}{\partial V}\right)_S = -\left(\frac{\partial G}{\partial V}\right)_T \quad [15]$$

$$V = \left(\frac{\partial H}{\partial P}\right)_S = \left(\frac{\partial G}{\partial P}\right)_T \quad [16]$$

$$T = \left(\frac{\partial E}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_P \quad [17]$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = -\left(\frac{\partial G}{\partial T}\right)_P \quad [18]$$

Taking second derivatives, the famous Maxwell relations are obtained:

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \quad [19]$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad [20]$$

$$\left(\frac{\partial T}{\partial P}\right)_S = -\left(\frac{\partial V}{\partial S}\right)_P \quad [21]$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \quad [22]$$

Using the Maxwell relations, a number of important thermodynamic relations are derived, for example,

$$\left(\frac{\partial S}{\partial V}\right)_T = \alpha K_T \quad [23]$$

$$\left(\frac{\partial S}{\partial V}\right)_P = \frac{C_P}{\alpha VT} \quad [24]$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\alpha V \quad [25]$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{\alpha VT}{C_P} \quad [26]$$

$$\left(\frac{\partial V}{\partial T}\right)_S = -\frac{C_P}{\alpha K_S T} \quad [27]$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \alpha K_T \quad [28]$$

In eqns [23]–[28], we used thermal expansion

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P \quad [29]$$

isothermal bulk modulus

$$K_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_S \quad [30]$$

and isobaric heat capacity

$$C_P = \left(\frac{\partial E}{\partial T}\right)_P \quad [31]$$

We note, on passing, that the bulk modulus and the heat capacity depend on the conditions of measurement. There are general thermodynamic equations relating the heat capacity at constant pressure (isobaric) and constant volume (isochoric)

$$C_P = C_V \left(1 + \frac{\alpha^2 K_T V}{C_V}\right) \quad [32]$$

and bulk modulus at constant temperature (isothermal) and at constant entropy (adiabatic):

$$K_S = K_T \left(1 + \frac{\alpha^2 K_T V}{C_P}\right) \quad [33]$$

The most interesting of eqns [23]–[28] are eqn [26], describing the increase of the temperature of a body on adiabatic compression (e.g., in shock waves and also inside rapidly convecting parts of planets), and eqn [28], describing thermal pressure. These equations are important for thermal equations of state and for calculating the temperature distributions inside planets.

2.08.1.3 Partition Function

Let us consider a system with energy levels E_i corresponding to the ground state and all the excited states. The probability to find the system in the i th state is proportional to $e^{-\beta E_i}$, where $\beta = 1/k_B T$ (k_B is the Boltzmann constant).

More rigorously, this probability p_i is given as

$$p_i = \frac{e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} \quad [34]$$

The denominator of this equation is called the partition function Z :

$$Z = \sum_i e^{-\beta E_i} \quad [35]$$

where the summation is carried out over all discrete energy levels of the system. The partition function is much more than a mere normalization factor; it plays a fundamental role in statistical physics, providing a link between the microscopic energetics and the macroscopic thermodynamics. Once Z is known, all thermodynamic properties can be obtained straightforwardly, for instance, the internal energy:

$$E = \sum_i p_i E_i = \frac{\sum_i E_i e^{-\beta E_i}}{Z} = -\frac{1}{Z} \left(\frac{\partial Z}{\partial \beta}\right)_V = -\left(\frac{\partial \ln Z}{\partial \beta}\right)_V \quad [36]$$

From this, one can derive a very important expression for the Helmholtz free energy

$$F = -\frac{1}{\beta} \ln Z = -k_B T \ln Z \quad [37]$$

entropy

$$S = k_B \ln Z - \frac{k_B \beta}{Z} \left(\frac{\partial Z}{\partial \beta}\right)_V \quad [38]$$

and the heat capacity at constant volume (from eqn [39], one can derive (see Dove, 2003) the following important formula ($C_V = k_B \beta^2 (\langle E^2 \rangle - \langle E \rangle^2)$):

$$C_V = -\frac{k_B \beta^2}{Z^2} \left(\frac{\partial Z}{\partial \beta}\right)_V^2 + \frac{k_B \beta^2}{Z} \left(\frac{\partial^2 Z}{\partial \beta^2}\right)_V \quad [39]$$

Unfortunately, in many real-life cases, it is practically impossible to obtain all the energy levels – neither experimentally nor theoretically – and therefore, the partition function cannot be calculated exactly. However, for some simplified models, it is possible to find the energy levels and estimate the partition function, which can then be used to calculate thermodynamic properties.

In the succeeding text, we consider the harmonic approximation, which plays a key role in the theory of thermodynamic properties of crystals. It gives a first approximation to the distribution of the energy levels E_i , which is usually accurate for the most populated lowest excited vibrational levels. The effects not accounted for by this simplified picture can often be included as additive corrections to the harmonic results.

2.08.1.4 Harmonic Approximation

The harmonic oscillator is a simple model system where the potential energy (U) is a quadratic function of the displacement x , for a simple diatomic molecule:

$$U(x) = U_0 + \frac{1}{2} k x^2 \quad [40]$$

where U_0 is the reference zero of energy and k is the force constant.

The energy levels of the harmonic oscillator can be found by solving the Schrödinger equation with the harmonic potential [40]; the result is an infinite set of equispaced energy levels:

$$E_n = \left(\frac{1}{2} + i\right) \hbar \omega \quad [41]$$

where $\hbar$ is the Planck constant, ω is the vibrational frequency of the oscillator, and integer i is the quantum number: $i=0$ for the ground state and $i \geq 1$ for excited states. Energy levels in a true vibrational system are well described by eqn [41] only for the lowest quantum numbers n , but these represent the most populated and thus the most important vibrational excitations.

A very interesting feature of eqn [41] is that even when $i=0$, that is, when there are no vibrational excitations (at 0 K), there is still a vibrational energy equal to $\hbar\omega/2$. This energy is called zero-point energy and arises from quantum fluctuations related to the Heisenberg uncertainty principle.

With eqn [41], the partition function for the harmonic oscillator is rather simple:

$$Z = \frac{1}{1 - e^{-\hbar\omega/k_B T}} \quad [42]$$

This allows one to calculate thermodynamic functions of a single harmonic oscillator (as was first done by Einstein):

$$E_{\text{vib}}(\omega, T) = \frac{1}{2} \hbar \omega + \frac{\hbar \omega}{\exp\left(\frac{\hbar \omega}{k_B T}\right) - 1} \quad [43]$$

$$C_{V,\text{vib}}(\omega, T) = k_B \left(\frac{\hbar \omega}{k_B T}\right)^2 \frac{\exp\left(\frac{\hbar \omega}{k_B T}\right)}{\left(\exp\left(\frac{\hbar \omega}{k_B T}\right) - 1\right)^2} \quad [44]$$

$$S_{\text{vib}}(\omega, T) = -k_B \ln \left[1 - \exp\left(-\frac{\hbar \omega}{k_B T}\right) \right] + \frac{1}{T} \frac{\hbar \omega}{\exp\left(\frac{\hbar \omega}{k_B T}\right) - 1} \quad [45]$$

$$F_{\text{vib}}(\omega, T) = \frac{1}{2} \hbar \omega + k_B T \ln \left[1 - \exp\left(-\frac{\hbar \omega}{k_B T}\right) \right] \quad [46]$$

The first term in eqn [43] is the zero-point energy originating from quantum motion of atoms discussed in the preceding text. The second temperature-dependent term gives the thermal energy of the mode according to the Bose–Einstein distribution. The thermal energy (or heat content) gives the energy absorbed by the crystal upon heating from 0 K to the temperature T . In the harmonic approximation, the isochoric C_V and isobaric C_P heat capacities are equal: $C_V = C_P$.

The number of phonons in a crystal containing N atoms in the unit cell is $3N$ (per unit cell). In the harmonic approximation, lattice vibrations do not interact with each other (in other words, propagation of one vibration does not change the energy or momentum of other vibrations), and their contributions to thermodynamic properties are additive. If all of the phonons had the same frequency (the assumption of the Einstein model), then, multiplying the right-hand sides of eqns [43]–[46] by the total number of vibrations $3N$, all thermodynamic properties would be obtained immediately.

However, normal-mode frequencies form a spectrum (called the phonon spectrum or phonon density of states $g(\omega)$); and an appropriate generalization [43]–[46] involves integration over all frequencies:

$$E_{\text{vib}}(T) = \int_0^{\omega_{\text{max}}} E_{\text{vib}}(\omega, T) g(\omega) d\omega$$

$$= \int_0^{\omega_{\text{max}}} \left(\frac{1}{2} \hbar \omega + \frac{\hbar \omega}{\exp\left(\frac{\hbar \omega}{k_B T}\right) - 1} \right) g(\omega) d\omega \quad [47]$$

$$C_{V,\text{vib}}(T) = \int_0^{\omega_{\text{max}}} C_{V,\text{vib}}(\omega, T) g(\omega) d\omega$$

$$= \int_0^{\omega_{\text{max}}} \left(k_B \left(\frac{\hbar \omega}{k_B T}\right)^2 \frac{\exp\left(\frac{\hbar \omega}{k_B T}\right)}{\left(\exp\left(\frac{\hbar \omega}{k_B T}\right) - 1\right)^2} \right) g(\omega) d\omega \quad [48]$$

$$S_{\text{vib}}(T) = \int_0^{\omega_{\text{max}}} S_{\text{vib}}(\omega, T) g(\omega) d\omega = \int_0^{\omega_{\text{max}}} \left(-k_B \ln \left[1 - \exp\left(-\frac{\hbar \omega}{k_B T}\right) \right] \right. \\ \left. + \frac{1}{T} \frac{\hbar \omega}{\exp\left(\frac{\hbar \omega}{k_B T}\right) - 1} \right) g(\omega) d\omega \quad [49]$$

$$F_{\text{vib}}(T) = E_0 + \int_0^{\omega_{\text{max}}} F_{\text{vib}}(\omega, T) g(\omega) d\omega$$

$$= E_0 + \int_0^{\omega_{\text{max}}} \left(\frac{1}{2} \hbar \omega + k_B T \ln \left[1 - \exp\left(-\frac{\hbar \omega}{k_B T}\right) \right] \right) g(\omega) d\omega \quad [50]$$

where E_0 is the energy of the static lattice.

2.08.1.4.1 Debye model

In early works, the phonon density of states $g(\omega)$ had often been simplified using the Debye model. For the acoustic modes, the phonon spectrum can be described, to a first approximation, as a parabolic function,

$$g(\omega) = 9N \left(\frac{\hbar}{k_B \theta_D} \right)^2 \omega^2 \quad [51]$$

truncated at the maximum frequency $\omega_D = k_B \theta_D / \hbar$, where θ_D is the Debye temperature.

With this $g(\omega)$ thermodynamic functions take the following forms:

$$E_{\text{vib}} = \frac{9}{8} k_B N \theta_D + 3 k_B N T D\left(\frac{\theta_D}{T}\right) \quad [52]$$

$$C_V(T) = \left(\frac{dE_{\text{vib}}}{dT} \right)_V = 3 k_B N \left[4 D\left(\frac{\theta_D}{T}\right) - \frac{3(\theta_D/T)}{e^{\theta_D/T} - 1} \right] \quad [53]$$

$$S(T) = \int_0^T \frac{C_P}{T} dT = k_B N \left[4 D\left(\frac{\theta_D}{T}\right) - 3 \ln \left(1 - e^{-\theta_D/T} \right) \right] \quad [54]$$

where $D(x) = (3/x^3) \int_0^x (x^3 dx) / (e^x - 1)$, $x = \theta_D/T$.

The first term in eqn [52] is the zero-point energy in the Debye model; the second term is the heat content. The Debye temperature is determined by the elastic properties of the solid – or, more precisely, its average sound velocity $\langle v \rangle$:

$$\theta_D = \frac{\hbar}{k_B} \left(\frac{6\pi^2 N}{V} \right)^{1/3} \langle v \rangle \quad [55]$$

The mean sound velocity can be accurately calculated from the elastic constant tensor (Robie and Edwards, 1966). Usually, however, an approximate formula is used:

$$\langle v \rangle = \left(\frac{1}{v_p^3} + \frac{2}{v_s^3} \right)^{-1/3} \quad [56]$$

where v_p and v_s are the longitudinal and transverse sound velocities, respectively. Later in this chapter, we shall see how to calculate these velocities. The advantages of the Debye model are its relative simplicity and correct low- and high-temperature limits for all thermodynamic properties. The crucial disadvantage is that it is still hardly able to give accurate entropies for anything other than monatomic lattices. Deep theoretical analyses of this model and its critique can be found in Seitz (1949) and Kieffer (1979). In Figure 2, we compare the phonon spectra and C_V obtained in the Debye model and in full-phonon harmonic calculations done with the same model interatomic potential (see Oganov et al., 2000). The phonon spectra are very different, but heat capacities are reasonably close (only below ~ 500 K, the disagreement is appreciable).

2.08.1.4.2 General harmonic potential

Let us now come back to the general harmonic case. First of all, the potential [40] describing a simple elastic spring or a diatomic molecule can be generalized to the case of three-dimensional structures. One can expand the crystal potential energy U around the equilibrium configuration in terms of displacements $u_\alpha^i(l)$ of i th atoms in the l th unit cell along each α th coordinate (Cartesian) axis:

$$U = U_0 + \sum_{l,i,\alpha} \Phi_\alpha^i(l) u_\alpha^i(l) + \frac{1}{2!} \sum_{l < l', i < j, \alpha, \beta} \Phi_{\alpha\beta}^{ij}(ll') u_\alpha^i(l) u_\beta^j(l') + \frac{1}{3!} \sum_{l < l' < l'', j < j' < k, \alpha, \beta, \gamma} \Phi_{\alpha\beta\gamma}^{ijk}(ll'l'') u_\alpha^i(l) u_\beta^j(l') u_\gamma^k(l'') + \dots \quad [57]$$

where

$$\begin{aligned} \Phi_\alpha^i(l) &= \frac{\partial U}{\partial u_\alpha^i(l)} \\ \Phi_{\alpha\beta}^{ij}(ll') &= \frac{\partial^2 U}{\partial u_\alpha^i(l) \partial u_\beta^j(l')} \\ \Phi_{\alpha\beta\gamma}^{ijk}(ll'l'') &= \frac{\partial^3 U}{\partial u_\alpha^i(l) \partial u_\beta^j(l') \partial u_\gamma^k(l'')} \end{aligned} \quad [58]$$

At equilibrium, $\Phi_\alpha^i(l) = 0$; so neglecting third- and higher-order terms (called anharmonic), we obtain the harmonic expansion of the potential energy:

$$U = U_0 + \frac{1}{2} \sum_{l < l', i < j, \alpha, \beta} \Phi_{\alpha\beta}^{ij}(ll') u_\alpha^i(l) u_\beta^j(l') \quad [59]$$

which is the analogue of our original simple model [40]. The generalized harmonic potential [57] includes noncentral forces, due to which directions of the displacement and force may differ. In spite of the complicated mathematical form of eqn [57], it is really analogous to eqn [40]. It also corresponds to a set of phonons, which are again noninteracting and have the same quantization as given by eqn [41].

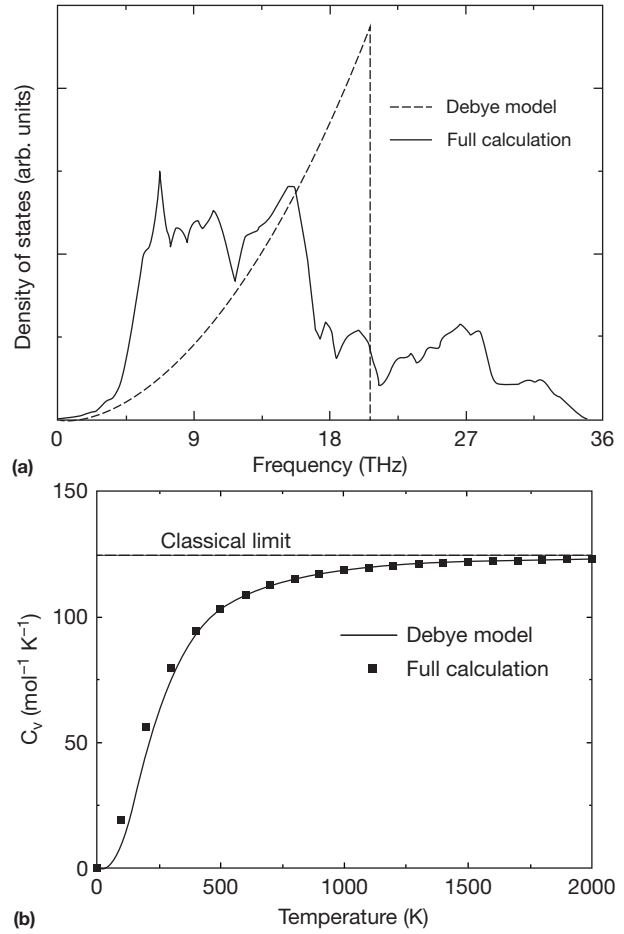


Figure 2 Phonon density of state (a) and heat capacity C_V of MgSiO_3 perovskite. Reproduced from Oganov AR, Brodholt JP, and Price GD (2000) Comparative study of quasiharmonic lattice dynamics, molecular dynamics and Debye model in application to MgSiO_3 perovskite. *Physics of the Earth and Planetary Interiors* 122: 277–288.

For each vibrational mode, the partition function is expressed as [42], and thermodynamic properties are described by eqns [47]–[50].

The harmonic approximation, neglecting third- and higher-order terms in the interatomic potential, leads to a number of fundamental errors. The phonon frequencies in this approximation do not depend on temperature or volume and are noninteracting. This leads to a simple interpretation of experimentally observed vibrational spectra and greatly simplifies the calculation of thermodynamic properties [47]–[50], but noninteracting phonons can freely travel within the crystal, leading to an infinite thermal conductivity of the harmonic crystal. In a real crystal, thermal conductivity is, of course, finite due to phonon–phonon collisions, scattering on defects, and finite crystal size. In the harmonic approximation, the energy needed to remove an atom from the crystal is infinite – therefore, diffusion and melting cannot be explained within this approximation. The same can be said about displacive phase transitions – even though the harmonic approximation can indicate such a transition by showing a soft mode, no properties can be calculated for the dynamically disordered

phase. In the harmonic approximation, there is no thermal expansion, which obviously contradicts experiment. Related to this is the equality $C_V = C_P$, whereas experiment indicates $C_V < C_P$ (see [32]). In a harmonic crystal, at high temperatures, C_V tends exactly to the Dulong–Petit limit of $3Nk_B$, whereas for anharmonic crystals, this is not the case.

The first approximation correcting many of these drawbacks, the quasiharmonic approximation (QHA), and methods to account for higher-order anharmonicity will be discussed later in this chapter, but now, let us explore some more fundamental aspects of thermodynamics.

2.08.1.5 Quantum Effects in Thermodynamics

Quantum effects are of fundamental importance for thermodynamic properties. Insufficiency of classical mechanics is apparent in any experimental determinations of the heat capacity at low temperatures.

According to classical mechanics, every structural degree of freedom has $k_B T/2$ worth of kinetic energy. In a harmonic solid, there is an equal amount of potential energy, so the total vibrational energy is equal to $3NRT$, and the heat capacity C_V is then $3NR$. In a stark contrast, experiment shows C_V going to zero as T^3 at low temperatures. Likewise, thermal expansion goes to zero at low temperatures – in contrast to classical theory, predicting a finite value. A very important consequence is for the entropy: if, as the classical approximation claims, $C_V = 3NR$ at all temperatures, then the entropy ($S = \int_0^T (C_V/T) dT$) is infinite.

The partition function [35] includes the relevant quantum effects, and so do harmonic expressions [43]–[50] for thermodynamic functions. In the classical approximation, the partition function is

$$Z_{\text{class}} = \frac{1}{N! \lambda^{3N}} \int \int e^{-\beta[U(r) + E_{\text{kin}}(p)]} dr dp \quad [60]$$

The denominator in this definition already accounts for some quantum effects. There, one has $N!$ to account for indistinguishability of same-type particles and λ^{3N} that takes into account the fact that quantum states are discrete and very small differences in coordinates/momenta of particles may correspond to the same quantum state. Nevertheless, this definition is classical – since it involves integration in the phase space, rather than summation over discrete quantum states, and since some essentially quantum effects (such as exchange) are not present in eqn [60].

According to the uncertainty principle, quantum particles are never at rest, and there is quantum motion of atoms even at 0 K called zero-point motion. The corresponding energy, arising from quantum motion in a potential field, is called the zero-point energy, which we already encountered in harmonic expressions [43], [46], [47], and [50]. The magnitude of zero-point motion is significant – it can contribute more than 50% of the total experimentally observed atomic mean-square displacements at room temperature.

It is important that at high temperatures, significantly exceeding the characteristic temperatures θ of all the vibrational modes ($\theta = \hbar\omega/k_B$), classical expressions will be correct. This circumstance justifies the application of methods based

on classical mechanics (molecular dynamics and Monte Carlo) in simulations of materials at high temperatures. At low temperatures, where quantum effects dominate, one could use the harmonic approximation (or, better, the QHA – see the succeeding text) or include quantum corrections to classical results.

The classical free energy can be calculated as

$$F_{\text{class}} = E_0 - k_B T \ln Z_{\text{class}} \quad [61]$$

The quantum correction to [61] per atom in the lowest order is (Landau and Lifshitz, 1980)

$$\begin{aligned} \Delta F = F - F_{\text{class}} &= \frac{\hbar^2}{24k_B^2 T^2} \left\langle \sum_i \frac{(\nabla_i U)^2}{m_i} \right\rangle \\ &= \frac{\hbar^2}{24k_B T} \left\langle \sum_i \frac{\nabla_i^2 U}{m_i} \right\rangle \end{aligned} \quad [62]$$

where ∇_i^2 is the Laplacian with respect to the coordinates of the i th atom. Higher-order ($\hbar^3$ and higher) corrections are needed only at temperatures below $\sim (\theta_D/2)$. Quantum corrections to other properties can be worked out by differentiating [62] – see Matsui (1989) and Figure 3.

Other possibilities to incorporate quantum corrections into classical results can be done using (1) path integral formalism (see Allen and Tildesley, 1987), (2) phonon density of states $g(\omega)$, which can be calculated classically, and quasiharmonic formulas. Montroll (1942, 1943) had formulated a method of calculating thermodynamic properties of a solid without the knowledge of $g(\omega)$ but using moments of the frequency distribution instead.

Defining the moments as

$$\mu_{2k} = \frac{1}{3N} \int_0^\infty \omega^{2k} g(\omega) d\omega \quad [63]$$

when $T > (\hbar\omega_{\text{max}}/k_B)$, one can write

$$E(T) = 3Nk_B T - 3Nk_B T \sum_{n=1}^\infty \frac{(-1)^n B_n}{(2n)!} \left(\frac{\hbar}{2k_B T} \right)^{2n} \mu_{2n} \quad [64]$$

$$C_V(T) = 3Nk_B - 3Nk_B \sum_{n=1}^\infty \frac{(-1)^n B_n (1-2n)}{(2n)!} \left(\frac{\hbar}{2k_B T} \right)^{2n} \mu_{2n} \quad [65]$$

where B_n are Bernoulli numbers. The first terms in eqns [64] and [65] are classical contributions; the second terms (sums) can be considered as quantum corrections. Taking only the first few terms, eqn [65] takes the following form:

$$C_V(T) \approx 3Nk_B \left[1 - \left(\frac{\hbar}{k_B T} \right)^2 \frac{\mu_2}{12} + \left(\frac{\hbar}{k_B T} \right)^4 \frac{\mu_4}{240} - \left(\frac{\hbar}{k_B T} \right)^6 \frac{\mu_6}{6048} + \dots \right] \quad [66]$$

The lowest-order quantum term is, as expected, of order $\hbar^2$.

2.08.1.6 Thermodynamic Perturbation Theory

It can be demonstrated (Landau and Lifshitz, 1980) that by modifying the potential energy of the system from U_0 to U_1 so that $V = U_1 - U_0$ is a small perturbation, to the first order, the free energy becomes

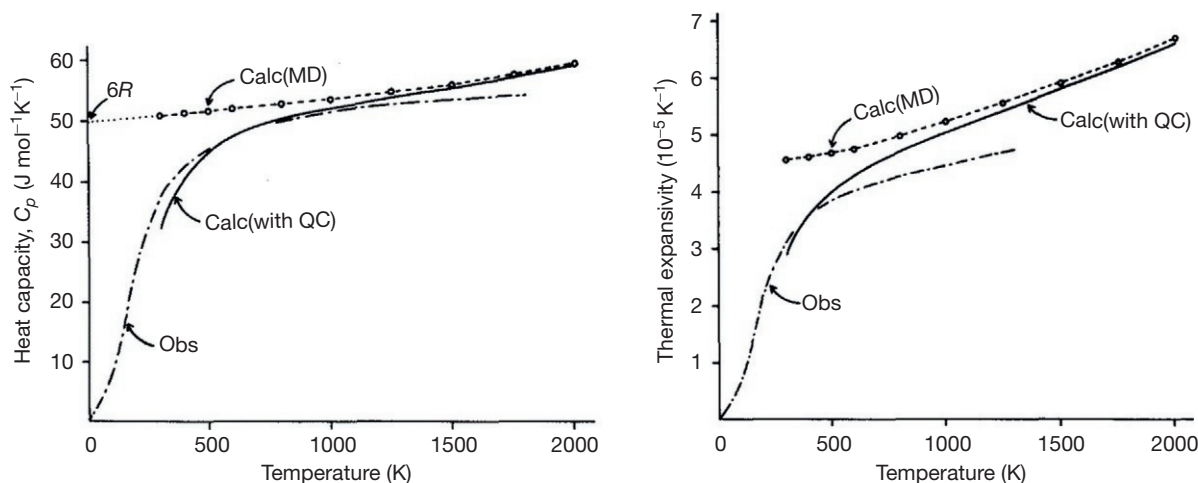


Figure 3 Heat capacity C_p and thermal expansion of MgO from classical molecular dynamics and with quantum corrections (5.3). Reproduced from Matsui M (1989) Molecular dynamics study of the structural and thermodynamic properties of MgO crystal with quantum correction. *Journal of Chemical Physics* 91: 489–494.

$$F_1 = F_0 + \langle V \rangle_0 \quad [67]$$

where subscript '0' means that averaging is performed over the configurations of the unperturbed system. This means that the free energy of a system with the potential U_1 can be found by thermodynamic integration from (any) system U_0 , the free energy of which is known:

$$F_1 = F_0 + \int_{\lambda=0}^1 U_\lambda d\lambda \quad [68]$$

where $U_\lambda = (1 - \lambda)U_0 + \lambda U_1$. The same ideology can be used for calculating the free energy profile along the chemical reaction coordinate or generally the free energy surface – as done in metadynamics simulations (Iannuzzi et al., 2003; Laio and Parrinello, 2002).

To second order, we have

$$F_1 = F_0 + \langle V \rangle_0 - \frac{1}{2k_B T} \langle (V - \bar{V})^2 \rangle_0 \quad [69]$$

where $\bar{V}$ is the averaged perturbing potential. Note that the expressions [67] and [69] are classical, but quantum extensions are available (Landau and Lifshitz, 1980). Thermodynamic perturbation theory plays an important role in methods to calculating free energies.

2.08.1.7 Quasiharmonic Approximation

In this approximation, it is assumed that the solid behaves like a harmonic solid at each volume, but the phonon frequencies depend on volume. It is assumed that they depend only on volume – that is, heating at constant volume does not change them.

In the QHA, phonons are still independent and non-interacting. Thermodynamic functions at constant volume, as before, are given by eqns [47]–[50]; C_V still cannot exceed 3NR. Melting, diffusion, and dynamically disordered phases

are beyond the scope of this approximation, which breaks down at high temperatures. Thermal conductivity is still infinite.

However crude, this approximation heals the biggest errors of the harmonic approximation. Introducing a volume dependence of the frequencies is enough to create nonzero thermal expansion and account for $C_V < C_p$ [32]. Thermal pressure contributes to all constant-pressure thermodynamic functions (enthalpy H , Gibbs free energy G , isobaric heat capacity C_p , etc.). This is the first approximation to the thermal equation of state of solids, which can be effectively used in conjunction with realistic interatomic potentials (Gale, 1998; Kantorovich, 1995; Parker and Price, 1989) or quantum-mechanical approaches (Baroni et al., 1987, 2001; Karki et al., 1999, 2000a,b; Oganov and Ono, 2004, 2005; Oganov and Price, 2005; Oganov et al., 2003, 2005a). It leads to some fundamental results, which remain almost intact in more accurate theories.

2.08.1.8 Beyond the QHA

At temperatures roughly below one-half to two-thirds of the melting temperature, QHA is quite accurate. Only at higher temperatures do its errors become significant. All the effects beyond the QHA are known as *intrinsic anharmonicity*. For instance, phonon–phonon interactions, displacive phase transitions, and explicit temperature dependence of the vibrational frequencies (which is experimentally measurable) are intrinsic anharmonic phenomena. Here, we focus on the role of intrinsic anharmonicity in thermodynamics and equations of state of solids, rather than on aspects related to thermal conductivity and phonon–phonon interactions.

The simplest way of treating intrinsic anharmonicity takes advantage of the fact that in the high-temperature expansion of the anharmonic free energy, the lowest-order term is quadratic (Gillet et al., 1999; Landau and Lifshitz, 1980; Zharkov and Kalinin, 1971). Explicit molecular dynamics simulations for MgO (Figure 4) show that third- and fourth-order terms still

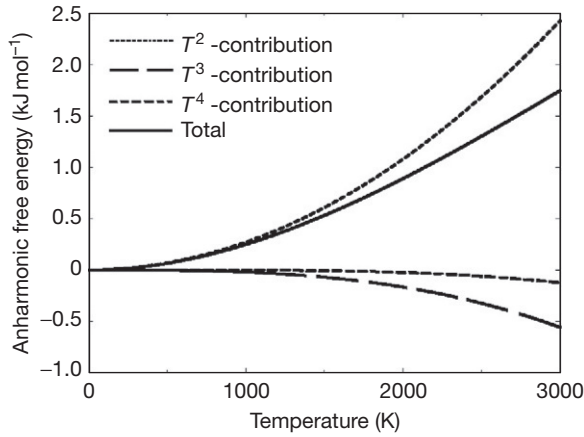


Figure 4 Intrinsic anharmonic free energy of MgO. Reproduced from Oganov AR and Dorogokupets PI (2004) Intrinsic anharmonicity in thermodynamics and equations of state of solids. *Journal of Physics: Condensed Matter* 16: 1351–1360.

play some role, but overall, the T^2 term dominates. Limiting ourselves to this term, we write

$$\frac{F_{\text{anh}}(V, T)}{3Nk_B} = \frac{1}{2}aT^2 \quad [70]$$

where a is the intrinsic anharmonicity parameter, usually of order 10^{-5} K^{-1} . Equation [70] assumes that intrinsic anharmonic contributions from different modes are additive. This is clearly a simplification, but it finds some justification in the arguments of Wallace (1998). Intrinsic anharmonicity normally decreases with pressure, which can be accounted for by a simple volume dependence (Zharkov and Kalinin, 1971):

$$a = a_0 \left(\frac{V}{V_0} \right)^m \quad [71]$$

where a_0 is the intrinsic anharmonicity parameter at standard conditions and $m = \frac{d \ln a}{d \ln V}$ is a constant.

One can easily find other anharmonic thermodynamic properties, such as the entropy, energy, isochoric heat capacity, thermal pressure, and bulk modulus:

$$\begin{aligned} \frac{S_{\text{anh}}}{3Nk_B} &= -aT, \quad \frac{E_{\text{anh}}}{3Nk_B} = -\frac{1}{2}aT^2, \quad \frac{C_{V,\text{anh}}}{3Nk_B} = -aT, \\ \frac{P_{\text{anh}}}{3Nk_B} &= -\frac{1}{2}a\frac{m}{V}T^2, \quad K_{Ta} = P_a(1-m) \end{aligned} \quad [72]$$

This model works well at high temperatures. However, at low temperatures, there are problems: linear anharmonic heat capacity [72] overwhelms the harmonic term, leading to large errors in the thermal expansion coefficient below $\sim 100 \text{ K}$. The problem is that [70] and [72] are classical equations and completely ignore quantum vibrational effects, which determine low-temperature thermodynamics.

Wallace (1998) had shown that in the first approximation, intrinsic anharmonic effects can be incorporated by using the true (i.e., temperature-dependent) vibrational frequencies ω (or characteristic temperatures $\theta = \hbar\omega/k_B$) and substituting them into the (quasi)harmonic expression for the entropy of a harmonic oscillator [45]. The result will contain both quasi-harmonic and intrinsic anharmonic contributions. We follow

Gillet et al. (1999) and define the temperature-dependent characteristic temperature as

$$\Theta_{VT} = \theta \exp(aT) \quad [73]$$

where θ is the quasiharmonic (only volume-dependent) characteristic temperature. Equation [73] thus defines the physical meaning of this parameter as the logarithmic derivative of the vibrational frequency (or characteristic temperature) with respect to volume:

$$a = \left(\frac{\partial \ln \omega_{VT}}{\partial T} \right)_V = \left(\frac{\partial \ln \Theta_{VT}}{\partial T} \right)_V \quad [74]$$

In the classical limit $\left(\frac{\Theta_{VT}}{T} \rightarrow 0 \right)$, eqns [70] and [72] are easily derived from eqn [74]. For the anharmonic free energy, Wallace's approach gives only the T^2 term; higher-order terms are absent.

Another approach to include quantum corrections in anharmonic properties is offered by thermodynamic perturbation theory of an anharmonic oscillator (Oganov and Dorogokupets, 2004). Consider a general anharmonic potential:

$$U_1 = \frac{1}{2}kx^2 + a_3x^3 + a_4x^4 + \dots \quad [75]$$

with $k > 0$.

As a reference system, we take a harmonic oscillator:

$$U_0 = \frac{1}{2}kx^2 \quad [76]$$

Using first-order thermodynamic perturbation theory [69], anharmonic free energy can be calculated as follows:

$$\begin{aligned} F_{\text{anh}} &= \langle U - U_0 \rangle_0 = \langle a_3x^3 + a_4x^4 + \dots \rangle_0 \\ &= a_4 \langle x^4 \rangle_0 + a_6 \langle x^6 \rangle_0 + a_8 \langle x^8 \rangle_0 + \dots \end{aligned} \quad [77]$$

This expression is remarkable in that the moments of atomic displacements used are those of a harmonic oscillator and can be easily calculated. Since the harmonic reference potential is symmetrical, only even-order terms are retained in eqn [77].

Truncating at the $\langle x^4 \rangle_0$ term, Oganov and Dorogokupets (2004) found

$$\frac{F_{\text{anh}}}{3n} = \frac{a}{6k_B} [\langle E \rangle^2 + 2k_B C_V T^2] \quad [78]$$

Other thermodynamic functions are easy to derive from F_{anh} by differentiation. From [78], one trivially obtains anharmonic zero-point energy:

$$\frac{E_{\text{anh}}^{\text{z.p.}}}{3n} = \frac{a}{24} k_B \theta^2 \quad [79]$$

For typical values of parameters ($a = 2 \times 10^{-5} \text{ K}^{-1}$, $\theta = 1000 \text{ K}$), this value amounts to only 0.17% of the harmonic zero-point energy. For more details on this formalism, see Oganov and Dorogokupets (2004).

Computationally, all intrinsic anharmonic effects can be fully accounted for by the use of Monte Carlo or molecular dynamics simulations (Allen and Tildesley, 1987): These methods involve a full sampling of the potential hypersurface without any assumptions regarding its shape or the magnitude of atomic vibrations; these methods are also applicable to

liquids and gases. Free energies of significantly anharmonic systems can be calculated using the thermodynamic integration technique (e.g., [Allen and Tildesley, 1987](#)).

2.08.2 Equations of State and Elasticity

Equations of state (i.e., the P - V - T relationship) of Earth-forming minerals are of special interest – indeed, accurate EOSs of minerals are necessary for the interpretation of seismological observations. The importance of the elastic constants for Earth sciences springs from the fact that most of the information about the deep Earth is obtained seismologically, by measuring the velocities of seismic waves passing through the Earth. Seismic wave velocities, in turn, are related to the elastic constants of Earth-forming rocks and minerals. Acoustic anisotropy of the Earth, measurable seismologically, is related to the elastic anisotropy of the Earth-forming minerals and the degree of their alignment.

2.08.2.1 Equations of State

Generally, thermodynamics gives

$$P = -\left(\frac{\partial F}{\partial V}\right)_T \quad \text{and} \quad V = \left(\frac{\partial G}{\partial P}\right)_T \quad \text{isothermal EOS}$$

$$T = \left(\frac{\partial H}{\partial S}\right)_P \quad \text{and} \quad S = -\left(\frac{\partial G}{\partial T}\right)_P \quad \text{isobaric EOS}$$

$$P = -\left(\frac{\partial E}{\partial V}\right)_P \quad \text{and} \quad V = -\left(\frac{\partial H}{\partial P}\right)_S \quad \text{adiabatic EOS}$$

An explicit analytic EOS can only be written for an ideal gas (where interatomic interactions are absent: In this case, there are no problems in the analytic representation of the interatomic potential, and entropy can be easily and exactly calculated using the Sackur–Tetrode relation).

For solids and liquids, interatomic interactions are essential, and all existing analytic EOSs are by necessity approximate. Even worse, interactions between atoms make phase transitions possible, and EOS becomes discontinuous (i.e., nonanalytic) at phase transitions. All the approximate EOS formulations are valid only for one phase (though for a phase transition involving only small structural changes, it is possible to formulate a single EOS describing two or more phases – see, e.g., [Tröster et al., 2002](#)), and generally, the accuracy of the EOS is best at conditions far from phase transitions.

2.08.2.1.1 Mie–Grüneisen EOS

To advance further, consider the isothermal EOS, $P = -(\partial F/\partial V)_T$, taking the QHA as the starting point. Using indices i and k to denote the number of the phonon branch and the wave vector $\mathbf{k}$, we can write a formula equivalent to [\[49\]](#):

$$F(T) = E_0 + \frac{1}{2} \sum_{i,k} \hbar \omega_{ik} + k_B T \sum_{i,k} \ln \left[1 - \exp\left(-\frac{\hbar \omega_{ik}}{k_B T}\right) \right] \quad [80]$$

From this, we have

$$P(V, T) = P_{st}(V) + \frac{1}{2} \sum_{i,k} \hbar \frac{\gamma_{ik} \omega_{ik}}{V} + \sum_{i,k} \frac{\gamma_{ik}}{V} \frac{\hbar \omega_{ik}}{\exp\left(\frac{\hbar \omega_{ik}}{k_B T}\right) - 1} \quad [81]$$

We have used in [\[81\]](#) the Grüneisen parameter:

$$\gamma_{ik} = -\left(\frac{\partial \ln \omega}{\partial \ln V}\right)_T \quad [82]$$

In the QHA, the Grüneisen parameter is temperature-independent.

At high temperatures or when all γ_{ik} are equal, [\[81\]](#) can be simplified:

$$P(V, T) = P_{st}(V) + \gamma \frac{E_{vib}(V, T)}{V} \quad [83]$$

where

$$\gamma = \langle \gamma_{ik} \rangle \quad [84]$$

Equation [\[83\]](#) is the famous Mie–Grüneisen thermal EOS. It should be noted that in the classical approximation, which is put in the basis of the standard molecular dynamics and Monte Carlo simulations, thermodynamic Grüneisen parameter will always be close to $\langle \gamma_{ik} \rangle$ ([Welch et al., 1978](#)) but will also include a temperature-dependent correction due to intrinsic anharmonic effects.

As shown by [Holzapfel \(2001\)](#), the three common definitions of the Grüneisen parameter (via the thermal pressure, thermal expansion, and volume derivatives of the phonon frequencies)

$$\gamma_P(V, T) = \frac{P_{vib}}{E_{vib}} V \quad [85a]$$

$$\gamma_\alpha(V, T) = \alpha \frac{K_T V}{C_V} \quad [85b]$$

$$\gamma_{qh}(V) = \left\langle -\frac{d \ln \omega_i}{d \ln V} \right\rangle \quad [85c]$$

are all identical in a classical quasiharmonic solid and all different in a system with intrinsic anharmonicity. Very roughly, $\gamma_P(V, T)$ is halfway between $\gamma_{qh}(V)$ and $\gamma_\alpha(V, T)$; that is, anharmonic effects are much more pronounced in thermal expansion than in thermal pressure. We stress that care must be taken as to which definition of the Grüneisen parameter is used when analyzing experimental and theoretical results. [Figure 5](#) shows the different definitions of the Grüneisen parameter and that the differences are small at low temperatures but significantly increase with temperature. There, we also show the volume dependence of the parameter q :

$$q = \left(\frac{\partial \ln \gamma}{\partial \ln V}\right)_T \quad [86]$$

Often, the volume dependence of γ is described by a power law:

$$\gamma(V) = \gamma_0 \left(\frac{V}{V_0}\right)^q \quad [87]$$

where parameter q is usually assumed to be constant. However, this form becomes poor at high compression. A much better function was proposed by [Al'tshuler et al. \(1987\)](#) (see also [Vorob'ev, 1996](#)):

$$\gamma = \gamma_\infty + (\gamma_0 - \gamma_\infty) \left(\frac{V}{V_0}\right)^\beta \quad [88]$$

where γ_0 and γ_∞ are Grüneisen parameters at $V=V_0$ and at infinite compression ($V=0$), respectively.

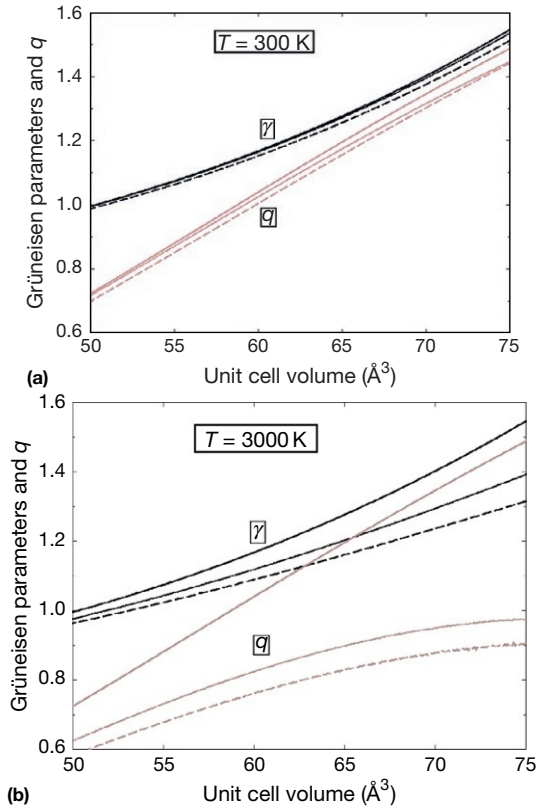


Figure 5 Grüneisen parameters and q parameter of MgO as a function of volume. (a) At 300 K, (b) at 3000 K. Solid lines, quasiharmonic results; dotted lines, γ_P ; dashed lines, γ_α . Reproduced from Oganov AR and Dorogokupets PI (2003) All-electron and pseudopotential study of MgO: Equation of state, anharmonicity, and stability. *Physical Review B* 67, art. 224110.

2.08.2.1.2 Analytic static EOS

Good discussions on this issue can be found in many sources, including Holzapfel (1996, 2001), Sutton (1993), Hama and Suito (1996), Cohen et al. (2000), Poirier (2000), and Vinet et al. (1986, 1989). Over decades, many different EOS forms have been generated, but here, we discuss only the ones that are most interesting from the theoretical and practical points of view.

The simplest approach is based on elasticity theory. Assuming that the bulk modulus K varies linearly with pressure and denoting $K'_0 = \left(\frac{\partial K}{\partial P}\right)_{P=0}$, we obtain the Murnaghan EOS:

$$P = \frac{K_0}{K'_0} \left[\left(\frac{V}{V_0} \right)^{-K'_0} - 1 \right] \quad [89]$$

This simple EOS works reasonably well only in a very limited compression range. Better (in terms of the accuracy relative to the number of parameters of the mathematical formulation) approach is provided by effective potential methods, where an approximate model for the energy as a function of $x = (V/V_0)$ or some other measure of strain.

For example, starting from a polynomial

$$E = E_0 + af^2 + bf^3 + cf^4 + \dots \quad [90]$$

in terms of the Eulerian strain f_E (It is advantageous to use the Eulerian finite strain rather than the Lagrangian strain $f_L = \frac{1}{2}[1 - x^{2/3}]$, because the Eulerian strain leads to a better description of the correct $E(V)$ dependence with fewer terms in the expansion [90]. At infinite pressure, Eulerian strain is infinite, whereas Lagrangian strain remains finite. However, for infinitesimal strains both definitions become equivalent.), $f_E = \frac{1}{2}[x^{-2/3} - 1]$, one arrives at the family of Birch–Murnaghan EOSs. Often used third-order Birch–Murnaghan EOS is

$$P = \frac{3}{2}K_0 \left[x^{-7/3} - x^{-5/3} \right] \left\{ 1 + \xi \left[x^{-2/3} - 1 \right] \right\} \quad [91]$$

$$E = E_0 + \frac{3}{2}K_0V_0 \left[\frac{3}{2}(\xi - 1)x^{-2/3} + \frac{3}{4}(1 - 2\xi)x^{-4/3} + \frac{1}{2}\xi x^{-6/3} - \frac{2\xi - 3}{4} \right] \quad [92]$$

where $\xi = \frac{3}{4}(K'_0 - 4)$.

It is possible to derive systematically higher-order BM EOS, but this appears to be of little use since the number of parameters involved will be too large; only the fourth-order BM EOS

$$P = 3K_0f_E(1 + 2f_E)^{5/2} \left\{ 1 + \frac{3}{2}(K'_0 - 4)f_E + \frac{3}{2} \left[K_0K''_0 + (K'_0 - 4)(K'_0 - 3) + \frac{35}{9}f_E^2 \right] \right\} \quad [93]$$

is sometimes used when ultrahigh pressures are studied.

The Vinet EOS (Vinet et al., 1986, 1989) is sometimes considered as one of the most impressive recent achievements in solid-state physics (Sutton, 1993). In fact, this is a whole family of EOSs of different orders. The most remarkable feature is very fast convergence with respect to the order of EOS – one seldom needs to use beyond the third-order Vinet EOS.

This EOS is based on a universal scaled binding curve:

$$E = E_0(1 + a)\exp(-a) \quad [94]$$

where E_0 is the bond energy at equilibrium, $a = (R - R_0)/l$, $l = \sqrt{E_0/(\partial^2 E/\partial R^2)}$ is a scaling length roughly measuring the width of the potential well, and R is the Wigner–Seitz radius (the average radius of a sphere in the solid containing 1 atom). The potential [94] was invented and first used by Rydberg (1932) for fitting potential curves of molecules and obtaining their anharmonic coefficients; it turned out (Vinet et al., 1986) that it describes very accurately systems with different types of chemical bonding in solids, molecules, adsorbates, etc.

The third-order Vinet EOS is (Hama and Suito, 1996; Vinet et al., 1989)

$$P = 3K_0 \frac{1 - x^{1/3}}{x^{2/3}} \exp \left[\eta \left(1 - x^{1/3} \right) \right] \quad [95]$$

$$E(V) = E(V_0) + \frac{9K_0V_0}{\eta^2} \left\{ 1 - \left[1 - \eta \left(1 - x^{1/3} \right) \right] \exp \left[\eta \left(1 - x^{1/3} \right) \right] \right\} \quad [96]$$

where $\eta = \frac{3}{2}(K'_0 - 1)$. The resulting expression for the bulk modulus is

$$K = \frac{K_0}{x^{2/3}} \left[1 + \left(1 + \eta x^{1/3} \right) \left(1 - x^{1/3} \right) \right] \exp \left[\eta \left(1 - x^{1/3} \right) \right] \quad [97]$$

From this, one has (Vinet et al., 1989)

$$K_0'' = -\frac{1}{K_0} \left[\left(\frac{K_0'}{2} \right)^2 + \left(\frac{K_0'}{2} \right) - \frac{19}{36} \right] \quad [98]$$

The Vinet EOS proved to be very accurate for fitting EOS of solid hydrogen (Cohen et al., 2000; Loubeyre et al., 1996) throughout the whole experimentally studied pressure range 0–120 GPa, roughly to the eightfold compression. The universal binding curve [94], however, does not describe long-range forces in ionic and van der Waals crystals. This means that for such material, Vinet EOS will not give accurate description of expansion ($x > 1$). For compression, however, it should be sufficiently accurate, since compression behavior is dominated by interatomic repulsion, well accounted for by [94].

In very rare cases, a higher-order Vinet EOS may be needed; such higher-order versions of the Vinet EOS already exist (Vinet et al., 1989),

$$P = \frac{3K_0}{x^{2/3}} \left(1 - x^{1/3} \right) \exp \left[\eta \left(1 - x^{1/3} \right) + \beta \left(1 - x^{1/3} \right)^2 + \gamma \left(1 - x^{1/3} \right)^3 + \dots \right] \quad [99]$$

and the fourth-order Vinet EOS, where $\beta = \frac{1}{24} (36K_0K_0'' + 9K_0'^2 + 18K_0' - 19)$ and $\gamma = 0$, has been successfully applied to solid H₂ at extreme compressions (Cohen et al., 2000) and has led to significant improvements of the description of experimental PV data.

In the limit of extreme compressions ($x \rightarrow 0$ (we do not consider here nuclear forces, which become important at densities $\sim 10^{15} \text{ g cm}^{-3}$ ($P \sim 10^{20} \text{ GPa}$) corresponding to $x < 10^{-12}$ (Holzapfel, 2001)), the Vinet EOS fails completely: it does not reproduce the correct free-electron limit and gives a finite (rather than positive infinite) energy equal to $\frac{9K_0V_0}{\eta^2} [1 - (1 - \eta)\exp(\eta)]$. EOSs, manifesting the correct Thomas–Fermi behavior at extreme compressions, have been developed and discussed in detail by Holzapfel (1996, 2001) and Hama and Suito (1996).

Holzapfel (1996, 2001) had modified the Vinet EOS so as to make it fulfill the electron-gas limit at extreme compressions. His APL EOS (also a family of L th-order EOSs) is as follows (Holzapfel, 2001):

$$P = \frac{3K_0}{x^{-5/3}} \left(1 - x^{1/3} \right) \exp \left[c_0 \left(1 - x^{1/3} \right) \right] \left\{ 1 + x^{1/3} \sum_{k=2}^L c_k \left(1 - x^{1/3} \right)^{k-1} \right\} \quad [100]$$

where $c_0 = -\ln \left(\frac{3K_0}{P_{\text{FG0}}} \right)$, $P_{\text{FG0}} = a_{\text{FG}} \left(\frac{Z}{V_0} \right)^{5/3}$, $a_{\text{FG}} = 0.02337 \text{ GPa } \text{\AA}^5$, and Z the total number of electrons per volume V_0 .

This EOS correctly predicts that at infinite compression, $K'_\infty = 5/3$ (while at $x = 1$, $K'_0 = 3 + \frac{3}{2}(c_0 + c_2)$) but becomes very similar to the Vinet EOS at moderate compressions.

The mathematical similarity between [99] and [100] is obvious, and it is easy to generalize these EOSs into one family. For a third-order generalized Vinet–Holzapfel EOS, one has (Kunc et al., 2003)

$$P = \frac{3K_0}{x^{n/3}} \left(1 - x^{1/3} \right) \exp \left[\eta \left(1 - x^{1/3} \right) \right] \quad [101]$$

where $\eta = \frac{3K_0'}{2} + \frac{1}{2} - n$. The Vinet EOS is recovered when $n = 2$, and the Holzapfel EOS is obtained when $n = 5$. Kunc et al. (2003) found that theoretical EOS of diamond is best represented by the EOS [101] with an intermediate value $n = 7/2$. In this case, the energy can be expressed analytically:

$$E(V) = E(V_0) + 9K_0V_0[f(V) - f(V_0)] \frac{\exp(\eta)}{\sqrt{\eta}} \quad [102]$$

where $f(V) = \sqrt{\pi}(2\eta + 1)\text{erf}(\sqrt{\eta}x^{2/3}) + \frac{2\sqrt{\eta}\exp(-\eta x^{1/3})}{x^{2/3}}$. However, it remains to be seen how accurate [102] is for other materials.

2.08.2.1.3 Anharmonicity in static EOS

Since both K' and γ come from anharmonic interactions, an intriguing possibility arises to establish a general relation between these parameters. This possibility was widely discussed since 1939, when J. Slater suggested the first solution of the problem:

$$\gamma_s = \frac{1}{2}K' - \frac{1}{6} \quad [103]$$

Later approaches resulted in very similar equations, the difference being in the value of the constant subtracted from $\frac{1}{2}K'$: $\frac{1}{2}$, $\frac{5}{6}$, or 0.95. If any of the relations of the type [103] were accurate, it would greatly simplify the construction of thermal EOS. Although some linear correlation between γ and K' does exist, the correlation is too poor to be useful (Wallace, 1998). Vočadlo et al. (2000) had examined all approximate theories of this kind and confirmed the conclusion of Wallace (1998).

2.08.2.1.4 EOS, internal strain, and phase transitions

All the EOSs discussed in the previous section were based on the assumption that crystal structures compress uniformly, and there is no relaxation of the unit cell shape or atomic relaxation. For some solids (e.g., MgO), this is definitely true. For most crystals and all glasses, however, this is an approximation, sometimes crude. All the classical EOSs are less successful for crystals with internal degrees of freedom. These EOSs perform particularly poorly in the vicinity of phase transitions. In the simplest harmonic model, Oganov (2002) obtained the following formula:

$$P(V) = P_{\text{unrelaxed}}(V) + \sum_i a_i^2 k_{0i} (V - V_0) \quad [104]$$

$P_{\text{unrelaxed}}$ is well described by the conventional EOSs, for example, Vinet EOS, whereas the total EOS is not necessarily so (see the succeeding text). The bulk modulus is always lowered by the relaxation effects, in the simplest approximation [104]:

$$K(V) = K_{\text{unrelaxed}}(V) - \sum_i a_i^2 k_{0i} V \quad [105]$$

which implies the tendency of K' to be higher than the corresponding unrelaxed value:

$$K'(V) = K'_{\text{unrelaxed}}(V) + \sum_i a_i^2 k_{0i} \frac{V}{K} \quad [106]$$

This simple model explains qualitatively correctly the real effects of internal strain. Complex structures are usually relatively 'soft' and usually have large K_0' (often significantly exceeding 'normal' $K_0' = 4$), in agreement with the prediction [106]. For example, quartz SiO_2 , although consisting of extremely rigid SiO_2 tetrahedra, has a very low bulk modulus $K_0 = 37.12$ GPa and high $K_0' = 5.99$ (Angel et al., 1997): its structure is very flexible due to relaxation of the internal degrees of freedom. Perhaps, the highest known $K_0' = 13$ was found in amphibole grunerite (Zhang et al., 1992) with a very complicated structure having many degrees of freedom.

As an illustration, consider two series of ab initio calculations on sillimanite, Al_2SiO_5 (based on results from Oganov et al., 2001b). In one series, all structural parameters were optimized, while in the other series, the zero-pressure structure was compressed homogeneously (i.e., without any relaxation). Results are shown in Figure 6, where a very large relaxation effects can be seen.

It is well known that internal strains always soften the elastic constants (e.g., Catti, 1989) and, in particular, the bulk modulus. In extreme cases (like the case of sillimanite), the softening can be complete, leading to a phase transition. In such cases, the simplified model [104] is not sufficient. To study EOS in the vicinity of the phase transition, one needs to go beyond the harmonic approximation built in this model. This can be done using the Landau expansion of the internal energy in powers of Q including the full elastic constants tensor and allowed couplings of the order parameter and lattice strains (see, e.g., Tröster et al., 2002).

2.08.2.2 Elastic Constants

A number of excellent books and reviews exist; I would emphasize Nye (1998), Sirotnin and Shaskolskaya (1975), Wallace (1998), Alexandrov and Prodaivoda (1993), Born and Huang (1954), Belikov et al. (1970), Barron and Klein (1965), and Fedorov (1968). Elastic constants characterize the ability of a

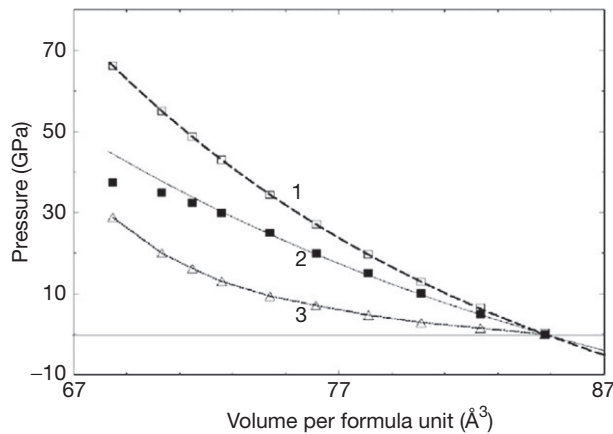


Figure 6 Effects of internal strains on equation of state. At the highest pressures shown, the structure is on the verge of an isosymmetric phase transition. 1, unrelaxed EOS; 2, correct EOS including relaxation; 3, the difference caused by relaxation. Note that in the pretransition region, the full EOS is poorly fit, while the unrelaxed EOS is very well represented by analytic EOSs (in this case BM3). Also note that the relaxational correction is very large.

material to deform under small stresses. They can be described by a fourth-rank tensor C_{ijkl} , relating the second-rank stress tensor σ_{ij} to the (also second-rank) strain tensor e_{kl} via the generalized Hooke's law:

$$\sigma_{ij} = C_{ijkl}e_{kl} \quad [107]$$

where multiplication follows the rules of tensor multiplication (see Nye, 1998). Equation [107] can be simplified using the Voigt notation (Nye, 1998), which represents the fourth-rank tensor C_{ijkl} by a symmetrical 6×6 matrix C_{ij} . In these notations, indices '11', '22', '33', '12', '13', and '23' are represented by only one symbol – 1, 2, 3, 6, 5, and 4, respectively. These notations significantly simplify all equations. So we write instead of [107]

$$\sigma_i = C_{ij}e_j \quad [108]$$

Note that infinitesimal strains are being used; in this limit, all definitions of strain (e.g., Eulerian, Lagrangian, and Hencky) become equivalent. Under a small strain, each lattice vector a_{ij}' of the strained crystal is obtained from the old lattice vector a_{ij}^0 and the strain tensor e_{ij} using the relation

$$a_{ij}' = (\delta_{ij} + e_{ij})a_{ij}^0 \quad [109]$$

In the original tensor notation and in the Voigt notation (Nye, 1998), the $(\delta_{ij} + e_{ij})$ matrix is represented as follows:

$$\begin{pmatrix} 1 + e_{11} & e_{12} & e_{13} \\ e_{12} & 1 + e_{22} & e_{23} \\ e_{13} & e_{23} & 1 + e_{33} \end{pmatrix} = \begin{pmatrix} 1 + e_1 & e_6/2 & e_5/2 \\ e_6/2 & 1 + e_2 & e_4/2 \\ e_5/2 & e_4/2 & 1 + e_3 \end{pmatrix} \quad [110]$$

Voigt notation is sufficient in most situations; only in rare situations such as a general transformation of the coordinate system, the full fourth-rank tensor representation must be used to derive the transformed elastic constants.

The number of components of a fourth-rank tensor is 81; the Voigt notation reduces this to 36. The thermodynamic equality $C_{ij} = C_{ji}$ makes the 6×6 matrix of elastic constants symmetrical, reducing the number of independent constants to the well-known maximum number of 21, possessed by triclinic crystals. Crystal symmetry results in further reductions of this number: 13 for monoclinic, 9 for orthorhombic, 6 or 7 (depending on the point-group symmetry) for trigonal and tetragonal, 5 for hexagonal, and 3 for cubic crystals; for isotropic (amorphous), solids there are only 2 independent elastic constants.

One can define the inverse tensor S_{ijkl} (or, in Voigt notations, S_{ij} (note that in Voigt notation, $C_{ijkl} = C_{mnr}$, but $S_{ijkl} = S_{mn}$ only when m and $n = 1, 2$, or 3 ; when either m or $n = 4, 5$, or 6 , $2S_{ijkl} = S_{mn}$; when both m and $n = 4, 5$, or 6 , $4S_{ijkl} = S_{mn}$ (Nye, 1998))), often called the elastic compliance tensor:

$$\{S_{ijkl}\} = \{C_{ijkl}\}^{-1} \text{ or } \{S_{ij}\} = \{C_{ij}\}^{-1} \quad [111]$$

The S_{ij} tensor can be defined via the generalized Hooke's law in its equivalent formulation:

$$e_i = S_{ij}\sigma_j \quad [112]$$

Linear compressibilities can be easily derived from the S_{ij} tensor. Full expressions for an arbitrary direction can be found in Nye (1998); along the coordinate axes, the linear compressibilities are

$$\begin{aligned}\beta_x &= -\frac{1}{l_x} \left(\frac{\partial l_x}{\partial P} \right)_T = \sum_{j=1}^3 S_{1j} = S_{11} + S_{12} + S_{13} \\ \beta_y &= -\frac{1}{l_y} \left(\frac{\partial l_y}{\partial P} \right)_T = \sum_{j=1}^3 S_{2j} = S_{12} + S_{22} + S_{23} \\ \beta_z &= -\frac{1}{l_z} \left(\frac{\partial l_z}{\partial P} \right)_T = \sum_{j=1}^3 S_{3j} = S_{13} + S_{23} + S_{33}\end{aligned} \quad [113]$$

where l_x, l_y, l_z are linear dimensions along the axes of the coordinate system. (These axes may not coincide with the lattice vectors for nonorthogonal crystal systems. Coordinate systems used in crystal physics are always orthogonal.) For the bulk compressibility, we have

$$\begin{aligned}\beta &= -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = \beta_x + \beta_y + \beta_z \\ &= \sum_{i=1}^3 \sum_{j=1}^3 S_{ij} = S_{11} + S_{22} + S_{33} + 2(S_{12} + S_{13} + S_{23})\end{aligned} \quad [114]$$

The values of the elastic constants depend on the orientation of the coordinate system. There are two particularly important invariants of the elastic constants tensor – bulk modulus K and shear modulus G . These are obtained by special averaging of the individual elastic constants. There are several different schemes of such averaging. Reuss averaging is based on the assumption of a homogeneous stress throughout the crystal, leading to the Reuss bulk modulus,

$$K_R = \frac{1}{S_{11} + S_{22} + S_{33} + 2(S_{12} + S_{13} + S_{23})} = \frac{1}{\beta} \quad [115]$$

and shear modulus,

$$G_R = \frac{15}{4(S_{11} + S_{22} + S_{33}) - 4(S_{12} + S_{13} + S_{23}) + 3(S_{44} + S_{55} + S_{66})} \quad [116]$$

It is important to realize that it is the Reuss bulk modulus, explicitly related to compressibility, that is used in constructing EOSs and appears in all thermodynamic equations involving the bulk modulus.

Another popular scheme of averaging is due to Voigt. It is based on the assumption of a spatially homogeneous strain and leads to the following expressions for the Voigt bulk and shear moduli:

$$K_V = \frac{C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23})}{9} \quad [117]$$

$$G_V = \frac{C_{11} + C_{22} + C_{33} - (C_{12} + C_{13} + C_{23}) + 3(C_{44} + C_{55} + C_{66})}{15} \quad [118]$$

For an isotropic polycrystalline aggregate, the Voigt moduli and the Reuss moduli give upper and lower bounds, respectively, for the corresponding moduli. More accurate estimates can be obtained from Voigt–Reuss–Hill averages:

$$\begin{aligned}K_{VRH} &= \frac{K_V + K_R}{2} \\ G_{VRH} &= \frac{G_V + G_R}{2}\end{aligned} \quad [119]$$

The most accurate results (and tighter bounds) are given by Hashin–Shtrikman variational scheme, which is much more complicated, but leads to results similar to the Voigt–Reuss–Hill scheme (see Watt et al., 1976 for more details).

There are two groups of experimental methods of measuring the elastic constants: (1) static and low-frequency methods (based on determination of stress–strain relations for static stresses) and (2) high-frequency, or dynamic, methods (e.g., ultrasonic methods and Brillouin spectroscopy). High-frequency methods generally enable much higher accuracy. Static measurements yield isothermal elastic constants (time-scale of the experiment allows thermal equilibrium to be attained within the sample); high-frequency measurements give adiabatic constants (Belikov et al., 1970). The difference, which is entirely due to anharmonic effects (see the succeeding text), vanishes at 0 K. Adiabatic C_{ij} are larger, usually by a few percent. The following thermodynamic equation gives the difference in terms of thermal pressure tensor b_{ij} (Wallace, 1998):

$$C_{ijkl}^S = C_{ijkl}^T + \frac{TV}{C_V} b_{ij} b_{kl} \quad [120]$$

where $b_{ij} = \left(\frac{\partial \sigma_{ij}}{\partial T} \right)_V$ is related to the thermal expansion tensor. Equation [120] implies for the bulk moduli the already-mentioned formula [33]:

$$K_S = K_T(1 + \alpha \gamma T) = K_T \left(1 + \frac{\alpha^2 K_T V}{C_V} \right)$$

where α and γ are the thermal expansion and Grüneisen parameter, respectively. Adiabatic and isothermal shear moduli are strictly equal for cubic crystals and usually practically indistinguishable for crystals of other symmetries.

Acoustic wave velocities measured in seismological experiments and ultrasonic determinations of elastic constants are related to the adiabatic elastic constants. Isothermal constants, on the other hand, are related to the compressibility and EOS.

The general equation for the calculation of velocities of acoustic waves with an arbitrary propagation direction, the Christoffel equation (Sirotn and Shaskolskaya, 1975), is

$$C_{ijkl}^S m_j m_k p_l = \rho v^2 p_i \quad [121]$$

where p is the polarization vector of the wave (of unit length), m the unit vector parallel to the wave vector, and ρ the density of the crystal. It can be also represented in a form of a secular equation:

$$\det \| C_{ijkl}^S m_j m_k - \rho v^2 \delta_{il} \| = 0 \quad [122]$$

This equation has three solutions, one of which corresponds to a compressional, and the other two to shear waves (see, e.g., Figure 7). For example, one can obtain the following velocities for a cubic crystal along high-symmetry directions:

$$\begin{aligned}\text{(a) } m \parallel [100]: & \quad v_1 = \sqrt{\frac{C_{11}}{\rho}} \quad (p = [100]), \quad v_2 = \sqrt{\frac{C_{44}}{\rho}} \quad (p = [010]), \\ & \quad v_3 = \sqrt{\frac{C_{44}}{\rho}} \quad (p = [001]), \\ \text{(b) } m \parallel [110]: & \quad v_1 = \sqrt{\frac{C_{11} + C_{12} + 2C_{44}}{2\rho}} \quad (p = [110]), \\ & \quad v_2 = \sqrt{\frac{C_{44}}{\rho}} \quad (p = [001]), \quad v_3 = \sqrt{\frac{C_{11} - C_{12}}{\rho}} \quad (p = [1\bar{1}0]),\end{aligned}$$

The average velocities are given by famous equations (Belikov et al., 1970):

$$v_p = \sqrt{\frac{3K + 4G}{3\rho}} \quad [123]$$

and

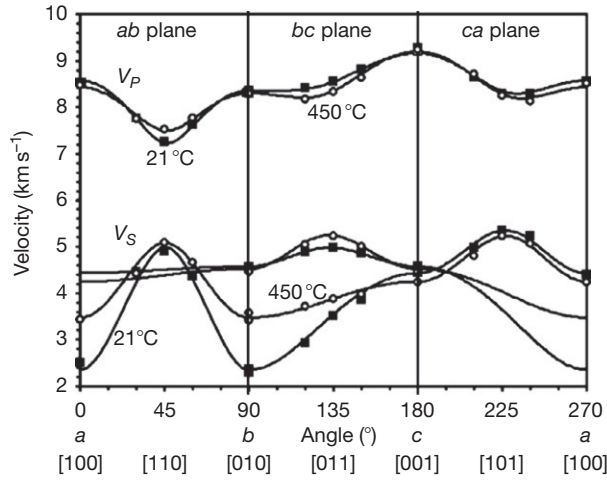


Figure 7 Acoustic velocities as a function of the propagation direction in lawsonite $\text{CaAl}_2(\text{Si}_2\text{O}_7)(\text{OH})_2 \cdot \text{H}_2\text{O}$. Solid squares, at 21 °C; open circles, 450 °C. Reproduced from Schilling FR, Sinogeikin SV, and Bass JD (2003) Single-crystal elastic properties of lawsonite and their variation with temperature. *Physics of the Earth and Planetary Interiors* 136: 107–118.

$$v_s = \sqrt{\frac{G}{\rho}} \quad [124]$$

where the adiabatic Voigt–Reuss–Hill (or Hashin–Shtrikman) values are used for the bulk and shear moduli.

At constant P , T , the elastic constants describing stress–strain relations [107] are given by

$$C_{ijkl}^T = \frac{1}{V} \left(\frac{\partial^2 G}{\partial e_{ij} \partial e_{kl}} \right)_T \quad [125]$$

while at constant P , S , they are

$$C_{ijkl}^S = \frac{1}{V} \left(\frac{\partial^2 H}{\partial e_{ij} \partial e_{kl}} \right)_S \quad [126]$$

Now, let us derive from eqn [125] an expression for the elastic constants in terms of the second derivatives of the internal energy; in this derivation, we follow Ackland and Reed (2003). The unit cell of a crystal can be represented by a matrix $\vec{V} = (\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)$, and the volume of the equilibrium unit cell is then $V_0 = \det \vec{V}$. Using [109], for the volume V of a strained cell, we obtain

$$\begin{aligned} \frac{V}{V_0} &= \frac{\det \vec{V}}{\det \vec{V}_0} \\ &= 1 + e_1 + e_2 + e_3 + e_1 e_2 + e_2 e_3 + e_1 e_3 - \frac{e_4^2}{4} - \frac{e_5^2}{4} \\ &\quad - \frac{e_6^2}{4} + e_1 e_2 e_3 - \frac{e_1 e_4^2}{4} - \frac{e_2 e_5^2}{4} - \frac{e_3 e_6^2}{4} + \frac{e_4 e_5 e_6}{4} \end{aligned} \quad [127]$$

Then, one has in the standard tensor notation

$$\frac{\Delta V}{V_0} = e_{ii} + \frac{1}{4} (2\delta_{ij}\delta_{kl} - \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}) e_{ij} e_{kl} + O(e^3) \quad [128]$$

The change of the Gibbs free energy associated with strain is then to the second order

$$\Delta G = \Delta F + P e_{ii} + \frac{P V}{4} (2\delta_{ij}\delta_{kl} - \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}) e_{ij} e_{kl} \quad [129]$$

From this, one has

$$C_{ijkl}^T = \frac{1}{V} \left(\frac{\partial^2 F}{\partial e_{ij} \partial e_{kl}} \right)_T + \frac{P}{2} (2\delta_{ij}\delta_{kl} - \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}) \quad [130a]$$

and, by analogy,

$$C_{ijkl}^S = \frac{1}{V} \left(\frac{\partial^2 E}{\partial e_{ij} \partial e_{kl}} \right)_S + \frac{P}{2} (2\delta_{ij}\delta_{kl} - \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}) \quad [130b]$$

It is well known (Barron and Klein, 1965; Wallace, 1998) that under nonzero stresses, there can be several different definitions of elastic constants. The constants C_{ijkl}^T and C_{ijkl}^S defined by eqns [130a] and [130b] are those appearing in stress–strain relations and in the conditions of mechanical stability of crystals (see the succeeding text), whereas the long-wavelength limit of lattice dynamics is controlled by $\frac{1}{V} \left(\frac{\partial^2 E}{\partial e_{ij} \partial e_{kl}} \right)_S$. These two definitions (via stress–strain relations and from long-wavelength lattice dynamics) become identical at zero pressure.

Calculating the second derivatives with respect to the finite Lagrangian strains η_{ij} , different equations are obtained (Wallace, 1998) for the case of hydrostatic pressure:

$$C_{ijkl}^S = \frac{1}{V} \left(\frac{\partial^2 E}{\partial \eta_{ij} \partial \eta_{kl}} \right)_S + P (\delta_{ij}\delta_{kl} - \delta_{il}\delta_{jk} - \delta_{jl}\delta_{ik}) \quad [131a]$$

$$C_{ijkl}^T = \frac{1}{V} \left(\frac{\partial^2 F}{\partial \eta_{ij} \partial \eta_{kl}} \right)_T + P (\delta_{ij}\delta_{kl} - \delta_{il}\delta_{jk} - \delta_{jl}\delta_{ik}) \quad [131b]$$

For a general stress, the analogous equations are

$$\begin{aligned} C_{ijkl}^S &= \frac{1}{V} \left(\frac{\partial^2 E}{\partial \eta_{ij} \partial \eta_{kl}} \right)_S \\ &\quad - \frac{1}{2} (2\sigma_{ij}\delta_{kl} - \sigma_{ik}\delta_{jl} - \sigma_{il}\delta_{jk} - \sigma_{jl}\delta_{ik} - \sigma_{jk}\delta_{il}) \end{aligned} \quad [132a]$$

$$\begin{aligned} C_{ijkl}^T &= \frac{1}{V} \left(\frac{\partial^2 F}{\partial \eta_{ij} \partial \eta_{kl}} \right)_T \\ &\quad - \frac{1}{2} (2\sigma_{ij}\delta_{kl} - \sigma_{ik}\delta_{jl} - \sigma_{il}\delta_{jk} - \sigma_{jl}\delta_{ik} - \sigma_{jk}\delta_{il}) \end{aligned} \quad [132b]$$

Cauchy relations, originally derived with the definition via the energy density, can be elegantly formulated in this definition as well (see the succeeding text). Note, however, that the elastic constants C_{ijkl} , defined from stress–strain relations, have the full Voigt symmetry only at hydrostatic pressure. It is essential to distinguish between different definitions of elastic constants under pressure.

2.08.2.2.1 Cauchy relations

For crystals where all atoms occupy centrosymmetric positions and where all interatomic interactions are central and pairwise (i.e., depend only on the distances between atoms and not on angles), the static limit Cauchy relations (Born and Huang, 1954; but take into account eq. 10.24) hold

$$\begin{aligned} C_{23} - C_{44} &= 2P; C_{31} - C_{55} = 2P; C_{12} - C_{66} = 2P \\ C_{14} - C_{56} &= 0; C_{25} - C_{64} = 0; C_{36} - C_{45} = 0 \end{aligned} \quad [133]$$

These relations would reduce the maximum number of independent elastic constants to 15; however, these relations never hold exactly because there are always noncentral and many-body contributions to crystal energy. Violations of the

Cauchy relations can serve as a useful indicator of the importance of such interactions. While for many alkali halides, Cauchy relations hold reasonably well, for alkali Earth oxides (e.g., MgO), also considered as classical ionic solids, Cauchy relations are grossly violated. This is because the free O^{2-} ion is unstable and can exist only in the crystalline environment due to the stabilizing Madelung potential created by all atoms in the crystal; the charge density around O^{2-} is thus very susceptible to the changes of structure, including strains. Consequently, interactions of the O^{2-} ion with any other ion depend on the volume of the crystal and location of all other ions; this is a major source of many-body effects in ionic solids. This point of view is strongly supported by the success of models such as PIB (potential-induced breathing; see Bukowski, 1994 and references therein), where the size of the atom depends on its Madelung potential, in reproducing the observed Cauchy violations.

2.08.2.2.2 Mechanical stability

One of the most common types of instabilities occurring in crystals is the so-called mechanical instability, when one or more elastic constants (or their special combinations) become zero. The condition of mechanical stability is the positive definiteness of the elastic constants matrix:

C_{11}	C_{12}	C_{13}	C_{14}	C_{15}	C_{16}
C_{21}	C_{22}	C_{23}	C_{24}	C_{25}	C_{26}
C_{31}	C_{32}	C_{33}	C_{34}	C_{35}	C_{36}
C_{41}	C_{42}	C_{43}	C_{44}	C_{45}	C_{46}
C_{51}	C_{52}	C_{53}	C_{54}	C_{55}	C_{56}
C_{61}	C_{62}	C_{63}	C_{64}	C_{65}	C_{66}

This is equivalent to positiveness of all the principal minors of this matrix (principal minors are square submatrices symmetrical with respect to the main diagonal – they are indicated by dashed lines in the scheme in the preceding text). All diagonal elastic constants C_{ii} are principal minors and, therefore, must be positive for all stable crystals. Dynamical stability criteria were first suggested by Born and Huang (1954) and are sometimes called Born conditions. In general form, they are analyzed in detail in (Fedorov, 1968; Sirotin and Shaskolskaya, 1975). For crystals of different symmetries, these conditions have been thoroughly analyzed by Cowley (1976) and Terhune et al. (1985). Mechanical stability criteria for crystals under stress must employ the C_{ij} derived from the stress-strain relations (Karki, 1997; Wang et al., 1993, 1995). Violation of any of the mechanical stability conditions leads to softening of an acoustic mode in the vicinity of the Γ -point, inducing a phase transition.

2.08.2.2.3 Birch's law and effects of temperature on the elastic constants

The famous Birch's law (Poirier, 2000) states that compressional sound velocities depend only on the composition and density of the material:

$$v_p = a(\bar{M}) + b(\bar{M})\rho \quad [134]$$

where $\bar{M}$ is the average atomic mass, a and b are constants, and ρ is the density. For example, for the mantle materials (average atomic mass between 20 and 22),

$$v_p = -1.87 + 3.05\rho \quad [135]$$

Similar relations hold for the bulk sound velocity $v_\Phi = \sqrt{\frac{K}{\rho}}$, for mantle compositions,

$$v_\Phi = -1.75 + 2.36\rho \quad [136]$$

Birch's law implies that for a given material at constant volume, the elastic constants are temperature-independent. This can be accepted only as a first (strictly harmonic) approximation. These contributions to the bulk modulus can be represented (Dorogokupets, 2000) as additive corrections to the zero-temperature result:

$$K^T(V, T) = K_{0K}(V) + \Delta K_{qha}^T(V, T) + \Delta K_a^T(V, T) \quad [137]$$

$$\Delta K_{qha}^T(V, T) = p_{th, qha}(1 + \gamma - q) - \gamma^2 TC_V/V \quad [138]$$

$$\Delta K_a^T(V, T) = p_a(1 + \gamma_a - q_a) \quad [139]$$

where $p_a = \gamma_a E_a/V$, $\gamma_a = -\left(\frac{\partial \ln a}{\partial \ln V}\right)_T$, and $q_a = \left(\frac{\partial \ln \gamma_a}{\partial \ln V}\right)_T$. For the adiabatic bulk modulus,

$$K^S(V, T) = K_{0K}(V) + p_{th, qha}(1 + \gamma - q) + p_a(1 + \gamma_a - q_a) \quad [140]$$

These results can be generalized for the individual elastic constants.

Garber and Granato (1975), differentiating the free energy expressed in the QHA as a sum of mode contributions over the whole Brillouin zone,

$$F = E_{st} + \frac{1}{2} \sum_{i,k} \hbar \omega_{ik} + \sum_{i,k} k_B T \ln \left[1 - \exp\left(-\frac{\hbar \omega_{ik}}{k_B T}\right) \right]$$

obtained the following result:

$$\begin{aligned} \frac{1}{V} \left(\frac{\partial^2 F}{\partial \eta_{ij} \partial \eta_{kl}} \right)_V &= \frac{1}{V} \left(\frac{\partial^2 E_{st}}{\partial \eta_{ij} \partial \eta_{kl}} \right)_V \\ &+ \frac{1}{V} \sum_{i,k} \left[\left(\gamma_{ij}^{ik, ik} \gamma_{kl}^{ik} - \frac{\partial \gamma_{ij}}{\partial \eta_{kl}} \right) E_{vib, ik} - \gamma_{ij}^{ik, ik} \gamma_{kl}^{ik} C_{V, ik} T \right] \end{aligned} \quad [141]$$

Section 2.08.3 gives an introduction to phase transitions. Some of the most important theoretical results and general ideas will be presented there. Crystal thermodynamics and elasticity, considered in this chapter, are among the key areas of interest in the study of phase transitions.

2.08.2.2.4 Elastic anisotropy in the Earth's interior

While most of the lower mantle and the entire outer core are elastically isotropic, seismological studies have indicated seismic anisotropy amounting to a few percent in the upper mantle, in the lowermost mantle (D'' layer), and in the inner core. This anisotropy can be due to lattice-preferred orientation (e.g., appearing due to plastic flow orienting crystallites in a rock) or due to their reasons such as shape-preferred orientation or macroscopic-scale ordered arrangements of crystals of different minerals and/or molten rock. The most interesting case is

lattice-preferred orientation. Elastic anisotropy causes splitting of seismic waves – much akin to birefringence of light waves in anisotropic crystals.

One would expect that crystals will orient their easiest plastic slip planes parallel to the direction of the flow. The selection of a single dominant slip plane is, of course, a simplification – which, however, leads to the most useful model of a transversely isotropic aggregate (where crystallites have parallel slip planes, but within the slip plane, their orientations are random). For the case of a transversely isotropic aggregate with a small degree of anisotropy, [Montagner and Nataf \(1986\)](#) considered the following parameters (the unique axis of the transversely isotropic aggregate is set to be *c*-axis):

$$\begin{aligned} A &= \frac{3}{8}(C_{11} + C_{22}) + \frac{1}{4}C_{12} + \frac{1}{2}C_{66} \\ C &= C_{33} \\ F &= \frac{1}{2}(C_{13} + C_{23}) \\ L &= \frac{1}{2}(C_{44} + C_{55}) \\ N &= \frac{1}{8}(C_{11} + C_{22}) - \frac{1}{4}C_{12} + \frac{1}{2}C_{66} \end{aligned} \quad [142]$$

From these, they derived the velocities of the shear vertically (v_{SV}) and horizontally (v_{SH}) and compressional vertically (v_{TV}) and horizontally (v_{TH}) polarized waves:

$$\begin{aligned} v_{PH} &= \sqrt{\frac{A}{\rho}} \\ v_{PV} &= \sqrt{\frac{C}{\rho}} \\ v_{SH} &= \sqrt{\frac{N}{\rho}} \\ v_{SV} &= \sqrt{\frac{L}{\rho}} \end{aligned} \quad [143]$$

What determines the dominant slip system? Strictly speaking, the dislocations – their number and the activation energy for their migration – should be the smallest for the best slip system. However, on the example of *hcp* metals, [Legrand \(1984\)](#) had demonstrated that a simplified criterion works very well. The product of the stacking fault enthalpy γ calculated per area S_{sf} ($\gamma = \Delta H_{sf}/S_{sf}$) and the shear elastic constant relevant for the motion of this stacking fault is smallest for the preferred slip plane. For example, comparing basal [0001] and prismatic [10 $\bar{1}$ 0] slip for *hcp* metals, the ratio

$$R = \frac{\gamma_{0001}C_{44}}{\gamma_{10\bar{1}0}C_{66}} \quad [144]$$

is greater than 1 in cases of prismatic slip and smaller than 1 for materials with basal slip.

2.08.3 Phase Transitions of Crystals

The study of phase transitions is of a central importance to modern crystallography, condensed matter physics and chemistry. Phase transitions are a major factor determining the seismic structure of the Earth and thus play a special role in geophysics (e.g., [Ringwood, 1991](#)).

2.08.3.1 Classifications of Phase Transitions

A popular classification of phase transitions was proposed by Ehrenfest in 1933 (for a historical and scientific discussion, see [Jaeger, 1998](#)), distinguishing between first-, second-, and higher-order phase transitions. For the *first-order* transitions, the *first* derivatives of the free energy with respect to *P* and *T* (i.e., volume and entropy) are discontinuous at the transition point; for *second-order* transitions, the *second* derivatives (compressibility, heat capacity, and thermal expansion) are discontinuous; and so forth. In some cases, the order of the same phase transition is different at different *P*–*T* conditions. Isosymmetric transitions must be first order but become completely continuous (infinite-order) transitions at and above the critical temperature. Some transitions change under pressure/temperature from the first to second order; the crossover point is called the tricritical point. Among the examples of systems with tricritical crossover are NH_4Cl ([Garland and Weiner, 1971](#)), zone-center cubic–tetragonal transition in BaTiO_3 perovskite, possibly the transition from calcite to metastable calcite (II) in CaCO_3 (see [Hatch and Merrill, 1981](#)), and, possibly, the α – β transition in quartz (SiO_2). For example, the order–disorder transition in NH_4Cl from a phase with a complete orientational disordering of the NH_4 group ($Pm\bar{3}m$) to an ordered phase ($P4\bar{3}m$) is first order at 1 atm and 242 K but becomes second order at the tricritical point, 0.15 GPa and 256 K. Therefore, the order of the transition is not something fundamentally inherent to the transition.

The first structural classification was due to [Buerger \(1961\)](#), who distinguished two main types of phase transitions – those with and without changes of the first coordination number, respectively. Each of these types was further classified into reconstructive (i.e., requiring formation/breaking of bonds), displacive, order–disorder, electronic, etc., transitions.

The beauty of the Buerger classification is that, even though based on purely structural considerations, it naturally gives some insight into thermodynamics and kinetics of phase transitions. For instance, reconstructive transitions are first order and require activation (and, hence, are kinetically controlled (polymorphs of carbon (graphite and diamond) and Al_2SiO_5 (minerals kyanite, andalusite, and sillimanite; see [Kerrick, 1990](#)) are classical examples. All the transitions between these minerals are first-order reconstructive and require substantial activation energies to proceed; therefore, all the three minerals can coexist at not very high temperatures for millions of years in nature)). Its weakness is in the absence of a precisely formulated quantitative basis. Formation/breaking of bonds is one of the main criteria. However, there is no rigorous physical definition of a chemical bond in a many-atom system. In many practical cases, it is very difficult to say whether or not two atoms in a given structure are linked by a bond or determine the coordination number of an atom in a crystal. This question is still an area of active research.

It was first realized by L. D. Landau in 1937 (see [Landau and Lifshitz, 1980](#)) that often, there are symmetry relations between the phases. Landau has shown that for a second-order transition, the two phases must be structurally related, and their symmetry groups must conform to certain group–subgroup relations.

2.08.3.2 First-Order Phase Transitions

Thermodynamics of first-order transitions are based on the Clausius–Clapeyron relation:

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} \quad [145]$$

where ΔS and ΔV are the entropy and volume differences, respectively, between the phases. Using [145], one can calculate the slopes of the equilibrium lines of phase coexistence. This relation is valid only for first-order transitions, because otherwise, both ΔV and ΔS are equal to zero. The transition temperatures and pressures can be found from accurate atomistic or quantum-mechanical total energy calculations (e.g., Oganov and Ono, 2004, 2005; Oganov et al., 2003, 2005a; Tsuchiya et al., 2004). Only when the two phases are structurally similar can one apply approximate analytic theories, such as Landau theory (which was initially devised to study second-order phase transitions).

A relation, analogous to [145], for second-order transitions was derived by Ehrenfest:

$$\frac{dP}{dT} = \frac{\Delta C_p}{TV\Delta\alpha} \quad [146]$$

where ΔC_p and $\Delta\alpha$ are the jumps of the heat capacity and thermal expansion at the transition. However, precise experiments, computer simulations, and accurate theories indicate a qualitatively different behavior of the heat capacity – instead of having a finite jump, it logarithmically diverges to infinity on both sides of the transition. This ‘ λ behavior’ invalidates the Ehrenfest relation.

2.08.3.3 Landau Theory of First- and Second-Order Transitions

When the structural changes occurring upon transition are small, it is usually possible to define an order parameter (or several order parameters), whose continuous change describes all the intermediate structures on the transition pathway. The simplest expression for the free energy is the Landau potential:

$$G(Q) = G_0 + \frac{1}{2}A(T - T_C)Q^2 + \frac{1}{3}BQ^3 + \frac{1}{4}CQ^4 + \dots \quad [147]$$

where T_C is the critical temperature and G_0 the free energy of the phase with $Q=0$ (e.g., high-temperature high-symmetry disordered phase). Landau’s assumption that the second term of [147] is simply proportional to $(T - T_C)$ was analyzed and justified mathematically within the mean-field theory by Sposito (1974). The entropy as a function of the order parameter is simply $S(Q) = -\partial G(Q)/\partial T = S_0 - (1/2)AQ^2$. This dependence of the entropy on the order parameter is most appropriate for displacive phase transitions. (For order–disorder transitions, the entropy is more accurately expressed as $S(Q) = S_0 - R[(1+Q)\ln(1+Q) + (1-Q)\ln(1-Q)]$.) The internal energy is then $E(Q) = E_0 - (1/2)AT_CQ^2 + (1/3)BQ^3 + (1/4)CQ^4 + \dots$. In the case $A > 0$, $B > 0$, and $C > 0$, this corresponds to a double-well potential $E(Q)$. (More than two minima can exist for higher-order polynomials [147].) For second-order transitions, the odd-order terms in [147] must be zero, making the double-well symmetrical. (This is only one of the necessary conditions. Other necessary conditions were formulated by Birman (1966) using group theory.)

Consider a second-order transition:

$$G(Q) = G_0 + \frac{1}{2}A(T - T_C)Q^2 + \frac{1}{4}CQ^4 + \dots \quad [148]$$

One can observe that at the transition point ($T = T_C$ and $Q = 0$), the second derivative of F with respect to Q changes sign, corresponding to freezing in of a soft mode below T_C and a corresponding structural distortion.

For first-order transitions, complete-mode softening does not occur at $T = T_C$.

Second-order phase transitions are always characterized by group–subgroup relations: the symmetry group of one (‘ordered,’ usually low-temperature) phase is a subgroup of the symmetry group of the other (‘disordered,’ usually high-temperature) phase. The two symmetrically equivalent minima then correspond to the same ordered phase and can be considered as ‘twin domains,’ related by a symmetry element present in the disordered phase, but absent in the ordered one (Figure 8).

The potential [147] is often complicated by the coupling of the order parameter to lattice strains. In such cases, the potential will be

$$G(Q) = \left(G_0 + \frac{1}{2}A(T - T_C)Q^2 + \frac{1}{3}BQ^3 + \frac{1}{4}CQ^4 + \dots \right) + a_1Q\epsilon + a_2Q\epsilon^2 + a_3Q^2\epsilon + 1/2C\epsilon^2 + \dots \quad [149]$$

where a_1 , a_2 , and a_3 are coupling coefficients and C is an elastic constant. Coupling of the order parameter to strains can cause a first-order behavior even for a symmetrical $E(Q)$.

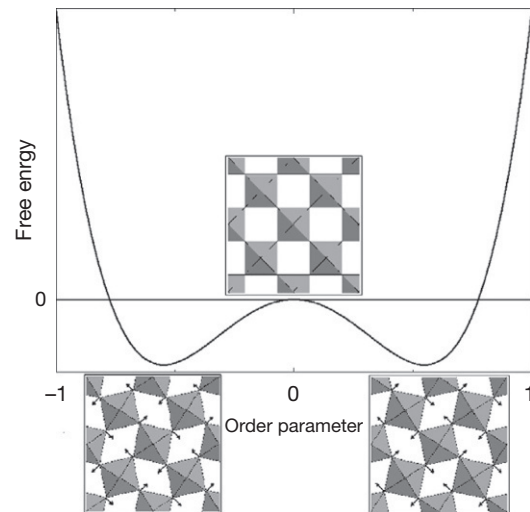


Figure 8 Symmetrical Landau potential at $T < T_C$. The two distorted perovskite-type structures shown on the bottom are equivalent (they are mirror reflections of each other); arrows show the directions of octahedral rotations away from the cubic structure. The undistorted structure is shown in the center. At temperatures higher than T_C , the stable structure will be locally distorted but on average will have the symmetry of the undistorted phase. Reproduced from Oganov AR, Brodholt JP, and Price GD (2002) Ab initio theory of thermoelasticity and phase transitions in minerals. EMU Notes in Mineralogy v. 4 (‘Energy Modelling in Minerals’, edited by C.M. Gramaccioli), pp. 83–170.

In some cases, more than one order parameter is required to describe a phase transition. Then, for the case of two order parameters, the Landau potential looks like

$$G(Q) = G(Q_1) + G(Q_2) + \xi_1 Q_1 Q_2 + \xi_2 Q_1^2 Q_2 + \xi_3 Q_1 Q_2^2 + \dots \quad [150]$$

where ξ_1 , ξ_2 , and ξ_3 are coupling coefficients for the Q_1 – Q_2 coupling. In cases where odd-order terms of the kind $\xi Q_1 Q_2 Q_3$ are present, the transition must be first order. For a detailed general account of Landau theory, see [Landau and Lifshitz \(1980\)](#), [Dove \(1993, 1997\)](#), [Carpenter et al. \(1998\)](#), and [Carpenter and Salje \(1998, 2000\)](#).

2.08.3.4 Shortcomings of Landau Theory

Landau theory belongs to a class of approximate theories known as mean-field theories. Mean-field treatment is a common way of approximately solving complex physical problems in many areas of science. The main drawback of these methods is the neglect of short-range fluctuations (in Landau theory, the local structure and fluctuations of the order parameter are neglected). In other words, Landau theory assumes that all the neighboring unit cells have the same configuration; therefore, domain structures and fluctuations of the order parameter in space and time are not treated. This problem becomes severe in the vicinity of T_C (in the so-called Ginzburg interval). For second-order transitions, Landau theory predicts $Q \sim (T_C - T)^{1/2}$, while experiments indicate $Q \sim (T_C - T)^{1/3}$. The critical exponent of $1/3$ has been many times confirmed by numerical computer simulations and could be explained only with the advent of renormalization group theory. (In fact, experiments give mean-field critical exponents far from T_C , but nearer to T_C , there is a crossover from the mean field to critical behavior, where the critical exponents depart significantly from the mean-field predictions.) The Landau theory cannot explain the logarithmic divergence of the heat capacity near the critical point – instead, it yields a finite jump. Finally, the Landau theory does not consider quantum effects at low temperatures. As a consequence, it does not reproduce experimentally observed order parameter saturation at low temperatures; instead, it predicts a steady increase of the order parameter with decreasing temperature.

2.08.3.5 Ginzburg–Landau Theory

In 1950, V. L. Ginzburg and L. D. Landau (see [Bowley and Sánchez, 1999](#); [Landau and Lifshitz, 1980](#)) considered the case of an order parameter slowly varying in space. This leads to the simplest theory beyond the mean field. The free energy becomes a *functional* of the order parameter, and an additional term proportional to the square of the gradient of the order parameter appears

$$F[Q(r)] = \int \left\{ f(Q(r)) + \frac{1}{2} \lambda [\nabla Q(r)]^2 \right\} dr \quad [151]$$

with the stiffness parameter $\lambda > 0$. For example, for a second-order transition,

$$F[Q(r)] = \int \left\{ \frac{1}{2} a(T - T_C) Q^2(r) + \frac{1}{4} b Q^4(r) + \frac{1}{2} \lambda [\nabla Q(r)]^2 \right\} dr \quad [152]$$

Then, Ginzburg and Landau expressed the order parameter as a sum of a constant term (the average order parameter) and fluctuations, which they expressed as a Fourier series:

$$Q(r) = \bar{Q} + \sum_k Q_k e^{ikr} \quad [153]$$

Equation [152] can be rewritten as

$$F[Q(r)] = \int \left\{ f(\bar{Q}) + Q_1(r) f' + \frac{1}{2} Q_1^2(r) f'' + \dots + \frac{1}{2} \lambda [\nabla Q(r)]^2 \right\} dr = V \left\{ f(\bar{Q}) + \frac{1}{2} \sum_k |Q_k|^2 (f'' + \lambda k^2) + \dots \right\} \quad [154]$$

Let us consider the case $f'' < 0$. In this case, the system is unstable against all fluctuations whose wave vectors satisfy $f'' + \lambda k^2 > 0$. Hence, the maximum unstable wave vector is $k_c = \sqrt{\frac{|f''|}{\lambda}}$. The correlation length ξ is

$$\xi = k_c^{-1} = \sqrt{\frac{\lambda}{|f''|}} \quad [155]$$

Ginzburg and Landau have proposed a criterion of the validity of Landau theory, defining the following value:

$$r(T) = \frac{f_m \xi^3}{k_B T} \quad [156]$$

where f_m is the difference of energies at the energy maximum and minimum. If $r(T) > 1$, fluctuations are not important, and Landau theory is valid. When $r(T) < 1$, fluctuations are essential and Landau theory is invalid; this occurs in the vicinity of T_C (this temperature region is called Ginzburg interval). Ginzburg intervals are usually quite narrow (of the order of ~ 10 K).

For second-order transitions, $f_m = \frac{a^2(T - T_C)}{4b}$ and

$$\xi = \sqrt{\frac{\lambda}{2a(T_C - T)}} \quad [157]$$

The Ginzburg–Landau theory emphasizes the role of critical fluctuations and defines criteria of validity of the Landau theory. However, this theory is still approximate and does not reproduce experimental critical exponents, for example, for the correlation length [157]. The renormalization group theory overcomes all these difficulties and serves as the modern basis of the theory of critical phenomena; applications of that theory extend well beyond the field of phase transitions and can be found in astronomy, engineering, and geology. The renormalization group theory goes beyond the mean-field approximation and fully treats all possible fluctuations of the order parameter. Introductory texts on this theory can be found in [Chandler \(1987\)](#), [Rao and Rao \(1978\)](#), and [Wilson \(1983\)](#); the latter reference is the Nobel lecture of Kenneth Wilson, one of its main inventors. This theory has led to the prediction of new physical phenomena, for example, continuous lattice melting, experimentally found in Na_2CO_3 ([Harris and Dove, 1995](#)).

2.08.3.6 Ising Spin Model

This model is widely used to describe magnetic and atomic ordering processes in materials. In this model, a spin $+1$ or -1

is associated with each lattice site, depending on whether the magnetic moment on the site is 'up' or 'down' or whether the atom occupying the site is of the type 'A' or 'B.'

The total energy of the system is

$$U = U_0 - J \sum_{i,j} s_i s_j - H \sum_i s_i \quad [158]$$

where U_0 is the reference energy and J the interaction parameter between the sites: If $J < 0$, unlike spins prefer to group together, and there is a tendency to ordering at low temperatures; if $J > 0$, unmixing will occur at low temperatures. Complete disorder, although unfavorable energetically, will be stabilized by the entropy at high temperatures. An external field H leads to a preferred orientation of the spins. The Ising model can be analytically solved only in one and two dimensions; for three dimensions, it is solved numerically, usually by the Monte Carlo method. The one-dimensional Ising model exhibits no phase transitions and at all temperatures above 0 K yields the disordered state.

Ising-like models provide an interesting route for theoretical studies of polytypism and polysomatism (see, e.g., Price, 1983; Price and Yeomans, 1984, and references therein). The crucial observation is the mathematical similarity between polytypic sequences (e.g., Figure 9) and one-dimensional Ising models.

The Ising model is also very attractive for studies of ordering processes (for a review, we refer the reader to Warren et al. (2001)) and can be generalized for the case of more than two spins (see Yeomans, 1992) – such variants will be applicable to ordering in multicomponent solid solutions and polytypic (polysomatic) systems with more than two types of layers.

The conventional Ising models assume that spins can be only 'up' or 'down,' and therefore, these models cannot be applied to noncollinear magnetic materials. For these cases, various Heisenberg models are appropriate, which take into account the orientations of the spins. The simplest of these models is based on the following Hamiltonian:

$$U = U_0 - J \sum_{i,j} \mathbf{s}_i \cdot \mathbf{s}_j - H \sum_i \mathbf{s}_i \cdot \mathbf{z} \quad [159]$$

involving spin vectors $\mathbf{s}_i$ and $\mathbf{s}_j$. Like the Ising model that had no phase transitions for one-dimensional systems, the Heisenberg model has no phase transitions for one- and two-dimensional systems.

2.08.3.7 Mean-Field Treatment of Order–Disorder Phenomena

The Bragg–Williams model is the simplest mean-field approach applicable to ordering phenomena. The free energy of the alloy as a function of temperature and order parameter is

$$G = G_0 - \frac{Nz}{4} J Q^2 + Nk_B T [(1+Q) \ln(1+Q) + (1-Q) \ln(1-Q)] \quad [160]$$

where G_0 is the free energy of the fully disordered state, N is the number of sites where disordering occurs, the order parameter $Q = X_{A,\alpha} - X_{A,\beta} = X_{B,\beta} - X_{B,\alpha} = 2X_{A,\alpha} - 1$, and the exchange energy $J = E_{AA} + E_{BB} - 2E_{AB}$.

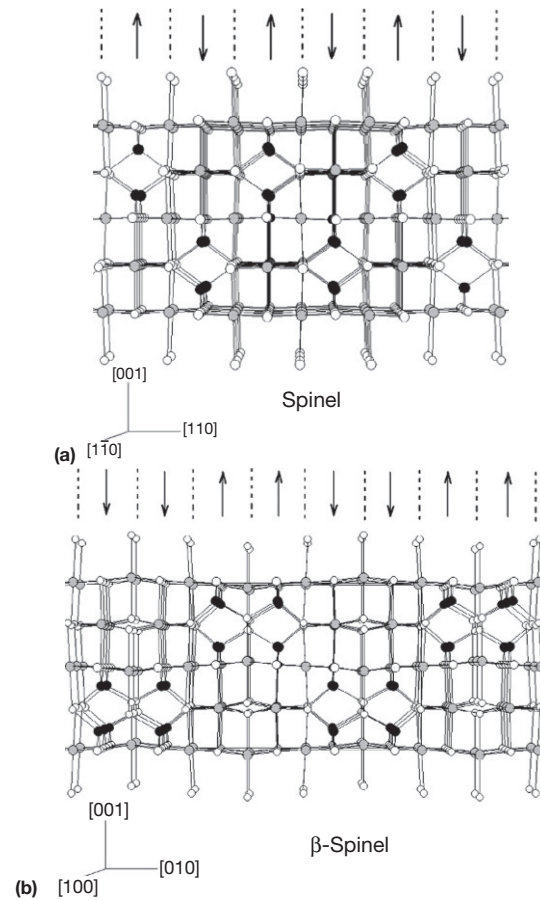


Figure 9 Polytypism in spinelloids. Structures of (a) spinel and (b) wadsleyite (β-spinel). Black circles are Si atoms (tetrahedrally coordinated), gray circles are Mg atoms (octahedrally coordinated), and empty circles are O atoms. Layers of different orientations are shown by 'up' and 'down' arrows highlighting the similarity with the one-dimensional Ising spin lattice. Spinelloids are interesting for Earth sciences, because of the phases of Mg_2SiO_4 – ringwoodite (spinel-like phase) and wadsleyite (β-spinel phase), which are the major constituents of the transition zone of the Earth's mantle.

The expression [160] is analogous to the Landau potential [148] and yields the same critical exponents. In three dimensions, this model gives qualitatively reasonable results; however, even with accurate exchange energies J , the predicted transition temperatures are usually a few times higher than the experimental ones (Redfern, 2000).

Drawbacks of the Bragg–Williams model can be corrected by explicitly considering short-range order. In the Bethe model (see Rao and Rao, 1978), apart from the long-range order parameter Q , one or more short-range order parameters are considered. These additional parameters describe the distribution of neighbors of both kinds in the nearest proximity of each atom. The resulting critical exponents and transition temperatures are much more realistic than the mean-field predictions.

In the succeeding text, we discuss features of different types of phase transitions, classified by their symmetry. This gives a new viewpoint on the variety of phenomena associated with phase transitions in solids.

2.08.3.8 Isosymmetric Transitions

Using the Landau theory, it is easy to show that isosymmetric transitions must be first order but can disappear (i.e., become fully continuous, infinite-order transitions) at the critical point and above it (Bruce and Cowley, 1981; Christy, 1995). There is a complete analogy here with the liquid–gas transitions (which are also isosymmetric). At supercritical temperatures, there are generally rapid but continuous changes in all properties along any P – T path going above the critical point (Angel, 1996).

Another example of isosymmetric phase transition phenomena outside the realm of solids is given by the newly discovered liquid–liquid phase transitions (McMillan, 2000), which are also first order with a critical point terminating the two-phase equilibrium line. A phase transition between structurally different amorphous phases (all liquid, gaseous, and conventional amorphous phases are isosymmetric, having spherical point-group symmetry) of ice was observed (Mishima et al., 1985) and reported to be first order. Increasingly, many crystals are now known to exhibit crystal–crystal isosymmetric phase transitions (i.e., those for which both phases have the same space group with the same number of atoms in the unit cell, with atoms occupying the same Wyckoff positions). Such transitions can be electronic (where the electronic structure changes, e.g., Ce and SmS), structural (where the coordination or ordering of the atomic species change discontinuously, e.g., KTiOPO_4), or intermediate (both electronic and structural changes are involved, e.g., Na_3MnF_6). Metallic Ce undergoes an isosymmetric phase transition Ce(I)–Ce(IV) (see Liu and Bassett, 1986 and references therein), presumably due to 6s–4f (or 5d) electronic transition. Both Ce(I) and Ce(IV) have the fcc structure (space group $Fm\bar{3}m$). The volume change at the transition is very large (13%) at room temperature, but it rapidly decreases along the Ce(I)–Ce(IV) equilibrium line until it disappears at the critical point (2.15 GPa and 613 K). Another famous example of an electronic transition is SmS, which transforms from the low-pressure insulating phase to the high-pressure metallic phase; both phases have a NaCl-type structure. Figure 10 explains this transition.

Structural isosymmetric crystal–crystal transitions do not involve any drastic changes in the electronic structure, but are purely atomistic. KTiOPO_4 (KTP) is known to undergo at 5.8 GPa a phase transition with a volume decrease of 2.7% with preservation of space group $Pna2_1$ (Allan and Nelmès, 1996). Large cages, occupied by K, lose 12% of their volume upon transition. KNO_3 (II)– KNO_3 (IV) phase transition, which occurs at 0.3 GPa and is accompanied by a volume decrease of 11.5%, does not alter the space group ($Pnma$) (Adams et al., 1988). Potassium atom coordination number changes from 9 to 11. An isosymmetric (space group $Pnam$) phase change has been observed at 9.8 GPa for PbF_2 (Haines et al., 1998) and involves a change of the coordination number of Pb atoms from 9 to 10. Na_3MnF_6 (space group $P2_1/n$) is an example of a phase transition with a simultaneous change in the atomic and electronic structure. At 2.2 GPa, this compound undergoes a first-order isosymmetric phase transformation, which is associated with a change of orientation of the Jahn–Teller elongation of MnF_6 octahedra (Carlson et al., 1998). The transformation shows a small hysteresis of 0.5 GPa. Zarechnaya et al. (2010) had ignored basic thermodynamics of isosymmetric transitions and, based on their experimental observations (which implied a second-order transition – perhaps also incorrectly), proposed an

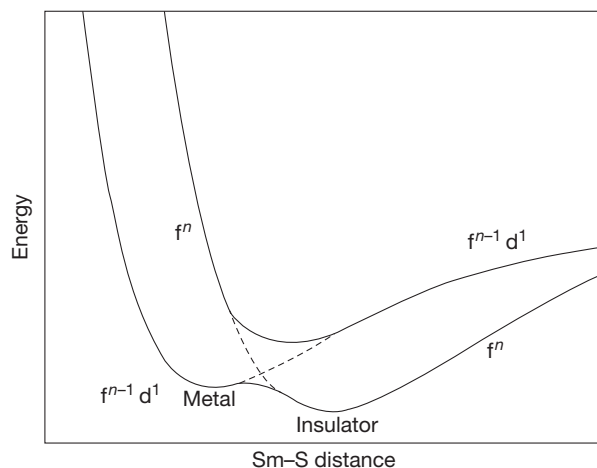


Figure 10 Illustration of the isosymmetric metal–insulator transition in SmS. Mixing of two configurations (metallic $f^{n-1}d$ and insulating f^n) produces a double-well energy curve for the ground state, where the minimum with a smaller interatomic distance corresponds to a metal. Compression triggers the insulator–metal transition. Modified from Burdett JK (1995) *Chemical Bonding in Solids*, p. 319. New York: Oxford University Press.

isosymmetric transformation in γ - B_{28} , the newly discovered (Oganov et al., 2009) high-pressure phase of boron. This instructive case was discussed by Le Godec et al. (2011).

2.08.3.9 Transitions with Group–Subgroup Relations

There are several possibilities here, stemming from different types of subgroups/supergroups of crystal symmetry. According to the Hermann theorem (Hahn and Wondratschek, 1994), a maximal subgroup of a space group is either *translationengleich* (German word meaning ‘having the same translations’; accepted as an international term (International Tables for Crystallography))–type (i.e., all translations are preserved, but some of the point-group symmetry operators disappear) or *klassengleich* (German word meaning ‘having the same (point-group) class’; accepted as an international term (International Tables for Crystallography))–type (i.e., all point-group operators are preserved, but some of the lattice translations disappear; as a consequence, a superstructure is formed). Subgroups, which are neither *klassengleich* nor *translationengleich*, are called *general* subgroups; they involve both cell multiplication and lowering of the point-group symmetry. Examples are $\alpha \rightarrow \beta$ quartz (*translationengleich*), $P2_1/c \rightarrow C2/c$ pyroxenes (*klassengleich*; see very interesting papers by Arlt and Angel (2000) and Arlt et al. (1998)), and $Pbnm \rightarrow Pm\bar{3}m$ transitions in perovskites (*general*).

The fourth type of transitions with group–subgroup transitions involves indirect symmetry relations between two phases via an intermediate archetypal phase of a higher symmetry, which is a supergroup for symmetries of both phases. An example is BaTiO_3 , where the transition between the rhombohedral and tetragonal phases can be described with reference to the higher-symmetry cubic phase. Such transitions are usually weakly first order.

Yet, another possibility is that of a transition state of a lower symmetry, which is a common subgroup of the symmetries of both phases. These transitions are usually strongly first order;

often, they can be described as reconstructive (see Christy, 1993). The fcc→bcc transition in Fe can be described with reference to lower-symmetry tetragonal or rhombohedral configurations, whose symmetries are common subgroups of both symmetry groups of the bcc and fcc phases.

2.08.3.10 Pressure-Induced Amorphization

This phenomenon, discovered in 1984 in experiments on compression of ice (Mishima et al., 1984) to 1 GPa at 77 K, attracts much interest due to its poor theoretical understanding and potential technological applications. Here, I give only a brief overview; for detailed reviews, see excellent papers (Richet and Gillet, 1997; Sharma and Sikka, 1996).

A great number of crystals undergoing pressure-induced amorphization (quartz SiO_2 , coesite SiO_2 , berlinite AlPO_4 , GeO_2 , zeolites scolecite $\text{Ca}_8\text{Al}_{16}\text{Si}_{24}\text{O}_{80} \cdot 24\text{H}_2\text{O}$ and mesolite $\text{Na}_{16}\text{Ca}_{16}\text{Al}_{48}\text{Si}_{72}\text{O}_{240} \cdot 64\text{H}_2\text{O}$, anorthite $\text{CaAl}_2\text{Si}_2\text{O}_8$, wollastonite CaSiO_3 , enstatite MgSiO_3 , muscovite $\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$, serpentine $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$, and portlandite $\text{Ca}(\text{OH})_2$ are just a few examples) and a few substances undergoing pressure-release amorphization, whereby high-pressure phases, when decompressed to pressures well below their stability fields, become dynamically unstable and amorphize, are known. (This happens to the perovskite-structured modification of CaSiO_3 , one of the main minerals of the Earth's lower mantle, which at ambient conditions turns to a glass within a few hours.)

Pressure-induced amorphization is always a metastable first-order transition. It requires that the amorphous phase be denser than the original crystalline phase. Thus, crystals with open structures should be easier to amorphize in contrast to close-packed ones. Pressure-induced amorphization occurs in the limit of dynamical stability of the crystal. In melting, the temperature of the onset of a mechanical instability gives an upper bound of the true thermodynamic melting temperature: solids cannot be overheated to higher temperatures.

Behavior of pressure-induced amorphous phases on decompression can be very different: Some compounds (e.g., $\text{Ca}(\text{OH})_2$) recrystallize; others (e.g., SiO_2 and ice) remain amorphous. Elastic anisotropy was found in pressure-amorphized quartz by Brillouin spectroscopy (McNeil and Grimsditch, 1991) and molecular dynamics simulations (Tse and Klug, 1993). The latter study found no structural relationships between pressure-amorphized quartz and silica glass.

The mechanisms driving pressure-induced amorphization are still not quite clear. The necessary conditions are the following: (1) Higher density of the amorphous phase relative to the crystal. Usually, it means that coordination numbers increase on amorphization. (2) Presence of soft modes in the crystalline phase. Softening of a vibrational mode at a single point of the Brillouin zone should drive a transition to a crystalline (if the soft wave vector is rational) or incommensurate (if the wave vector is irrational) phase. Simultaneous or nearly simultaneous softening of a phonon branch at a range of k -vectors (e.g., along a special direction of the Brillouin zone) could produce an amorphous phase (Binggeli et al., 1994; Hemmati et al., 1995; Keskar et al., 1994). Any atomic displacement, expressible as a combination of soft modes, lowers the energy; the multitude of possible combinations gives rise to the disorder. However, a large degree of order

should remain: because the displacements are expected to be small and because only displacements related to the softening phonon branch are allowed to freeze in. Simultaneous softening of a phonon branch along a direction in the Brillouin zone implies weak dispersion of this branch, which is most naturally achieved when the unit cell is large. Indeed, crystals with complicated structures and large unit cells are more prone to pressure-induced amorphization.

2.08.4 A Few Examples of the Discussed Concepts

Very briefly, we will discuss some recent results illustrating the use of the notions, discussed in the succeeding text. These include the calculation of the temperature profile of the Earth's lower mantle and core, polytypism of MgSiO_3 postperovskite and seismic anisotropy of the Earth's D'' layer, and spin transition in (Mg,Fe)O magnesiowüstite.

2.08.4.1 Temperature Profile of the Earth's Lower Mantle and Core

Equation [26] can be rewritten, taking into account eqn [85b], as follows:

$$\left(\frac{\partial \ln T}{\partial \rho}\right)_S = \gamma_\alpha \quad [161]$$

This formula describes adiabatic change of temperature upon compression and is relevant for first-order estimates of the average temperature distribution in convecting the mantle (where superadiabatic effects might be nonnegligible) and outer core (which is very closely adiabatic). Ab initio calculations of Alfè et al. (2002) produced an estimate of the temperature at the inner–outer core boundary (5150 km depth) of 5600 K. This was calculated from the melting curve of iron, taking into account the effect of impurities (Si, S, and O). While within the inner core, the temperature is likely to be constant, the temperature distribution in the outer core is adiabatic [161]. With their estimates of the Grüneisen parameter of liquid iron at relevant pressures and temperatures, Alfè et al. (2002) calculated the temperature distribution in the outer core. In particular, the core temperature at the boundary with the mantle was estimated to be in the range 4000–4300 K.

Phase-equilibrium experiments of Ito and Katsura (1989) produced another 'anchor' point for the calculation of the geotherm – 1873 K at the depth of 670 km (top of the lower mantle). Taking into account the Grüneisen parameters of MgSiO_3 perovskite and MgO periclase obtained in their ab initio simulations, Oganov et al. (2002) had calculated the adiabatic geotherm of the lower mantle. The resulting mantle temperature at the boundary with the core (2891 km depth) is 2700 K, indicating a strong thermal boundary layer with rapid temperature variations at the bottom of the mantle. Lateral temperature variations in the lower mantle (Oganov et al., 2001a) do indeed become large near the core–mantle boundary. These conclusions were fully confirmed by van der Hilst et al. (2007), who used the postperovskite transition to infer a 'cold' anomaly of -700 ± 100 K and a much larger 'hot' anomaly in the D'' layer, with 1400–1600 K temperature increase across the thermal boundary layer and the temperature at core–mantle boundary estimated as 3950 ± 200 K.

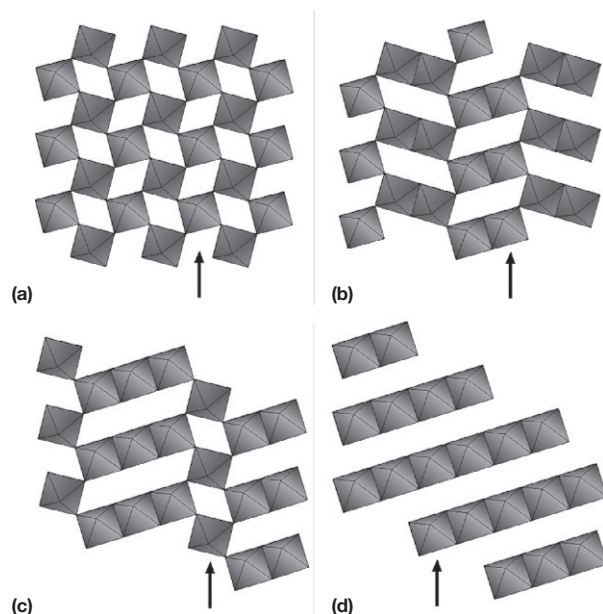


Figure 11 MgSiO_3 polytypes: (a) perovskite (space group $Pbnm$); (d) postperovskite ($Cmc21$); (b, c) intermediate structures 2×2 ($Pbnm$) and 3×1 ($P21/m$), respectively. Only silicate octahedra are shown; Mg atoms are omitted for clarity. Arrows indicate the predicted slip planes in these structures. Reproduced from Oganov AR, Martoňák R, Laio A, Raiteri P, and Parrinello M. (2005) Anisotropy of Earth's D'' layer and stacking faults in the MgSiO_3 post-perovskite phase. *Nature* 438: 1142–1144.

2.08.4.2 Polytypism of MgSiO_3 Postperovskite

Recently, Oganov et al. (2005b) found that MgSiO_3 perovskite and postperovskite can be considered as end members of an infinite polytypic series (Figure 11) – this is a case of non-traditional polytypism (for another illustration see Figure 9), since the ‘layers,’ whose shifting produces all the structures is the polytypic series, are not weakly bound and are not even immediately obvious in the structure. All these structures are energetically very similar, and since intermediate structures have only marginally higher enthalpies than perovskite or postperovskite, these phases could be stabilized by temperature and/or impurities in the Earth’s lowermost mantle.

2.08.4.3 Spin Transition in (Mg,Fe)O Magnesio-wüstite

Iron impurities play a large role in determining the properties of Earth-forming minerals. One particular complication arising from the presence of these impurities is the possible pressure-induced transition of Fe^{2+} (or Fe^{3+}) impurities from the high-spin state to the low-spin state. Typically, crystal fields induced by O^{2-} ions at low pressures are weak, and transition metal ions prefer to adopt the high-spin configurations (like in free ions). However, under pressure, the increasing crystal field and the additional PV term in the free energy prompt these ions to adopt much more compact low-spin forms (it is well documented that ionic radii are much larger for high-spin ions than for low-spin ones – e.g., Shannon and Prewitt, 1969). Recent studies of such a transition in (Mg,Fe)O magnesio-wüstite (Badro et al., 2003; Lin et al., 2005) demonstrated that this

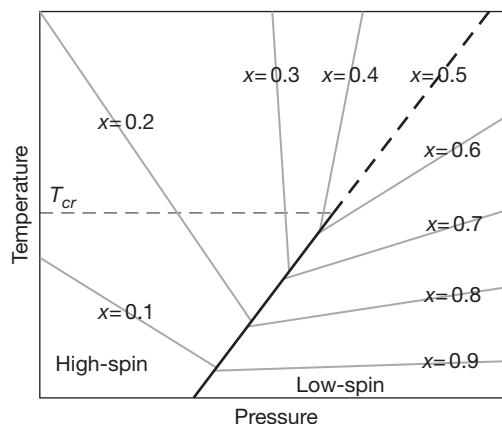


Figure 12 Schematic phase diagram for a system with a spin transition, for example, (Mg,Fe)O. Thick solid line: first-order transition, thick dashed line: continuous transition. Gray lines show the degree of spin miscibility (numbers: concentration of low-spin species relative to the total number of iron atoms). Above T_{cr} , the transition is fully continuous.

transition can have large effects of physical properties and could even have some global geophysical implications.

This spin transition is isosymmetric, and as such, it must (see Section 2.08.3) be first order at low temperatures and fully continuous above some critical temperature T_{cr} . While at 0 K, the low-pressure phase will contain only high-spin Fe^{2+} ions and only low-spin ions will be present in the high-pressure phase, on increasing temperature, there will be an increased degree of coexistence of the two spin states in the same phase – as a consequence, the first-order character of the transition decreases with temperature. At T_{cr} , the miscibility of high- and low-spin ions becomes complete, and the transition becomes fully continuous (infinite order, rather than first or second order); T_{cr} is proportional to the enthalpy that arises from the deformation of the structure due to insertion of a ‘wrong’-spin ion. While quantitative aspects of this transition were recently studied by different groups with various approximations (Sturhahn et al., 2005; Tsuchiya et al., 2006), the most important qualitative features (in addition to those mentioned in the preceding text) are immediately clear:

- Large positive Clapeyron slope (since magnetic entropy is much higher in the high-spin state).
- Low T_{cr} , perhaps several hundred Kelvin, since for relevant compositions (e.g., $\text{Mg}_{0.8}\text{Fe}_{0.2}\text{O}$), the energetic effects of Fe incorporation and the enthalpy of ‘spin mixing’ will be rather small. At lower mantle temperatures, the transition is likely to be continuous. A schematic phase diagram is given in Figure 12.

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2.09 Lattice Vibrations and Spectroscopy of Mantle Phases

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Outline

Vibrational spectroscopic techniques, including Raman, infrared (IR), and inelastic neutron scattering (INS) or x-ray scattering (IXS) spectroscopies, are coupled with *ab initio* or first principles calculations to study the vibrational lattice dynamics and to predict and elucidate the thermodynamic behavior of minerals under high-pressure–high-temperature conditions relevant to the Earth's mantle and other deep planetary interiors. Principal lower mantle and transition zone phases are (Mg,Fe)O magnesio-wüstite, silicate perovskite, majorite, wadsleyite, ringwoodite, and SiO₂ stishovite. They result from high-pressure transformation of olivine, pyroxene, and garnet phases that occur mainly within the upper mantle. Phase transformations in aluminous and hydrous mineral phases are also discussed.

2.09.1 Introduction

2.09.1.1 Deep Earth Mineralogy and Mineral Physics

Although mantle mineralogy is sampled directly to a certain depth by xenoliths brought to the surface and by phases contained inside inclusions within high-pressure minerals including diamonds (Boyd and Meyer, 1979; Dawson, 1980; Harris, 1992; Harte and Harris, 1994; Liou et al., 1998; McCammon

et al., 1997; Moore and Gurney, 1985; Nixon, 1987; Sautter et al., 1991), our main understanding of deep Earth mineralogy and the physical properties of the deep Earth is derived from seismology and cosmochemistry, combined with experimental and theoretical mineral physics (Anderson, 1989; Birch, 1952; Hemley, 1998; Ringwood, 1975).

The Earth's upper mantle is dominated by ultramafic phases, principally olivines (α -(Mg,Fe)₂SiO₄), pyroxenes, and garnets. Minor phases including plagioclase feldspar, kaersutite amphibole, and phlogopite mica also occur (McDonough and Rudnick, 1998). Some of these phases are volatile-rich, providing hosts and sinks for OH/H₂O and CO₂ species, as well as F, Cl, and S, either being returned to the mantle *via* subduction processes or degassing from primary materials deep within the Earth (Bell and Rossman, 1992; Carroll and Holloway, 1994; Gasparik, 1993; Thompson, 1992).

The mantle transition zone is dominated by the mineralogy of refractory ultramafic minerals including β -(Mg,Fe)₂SiO₄ wadsleyite (also known in earlier works as 'beta-phase,' or 'modified spinel') and spinel-structured γ -(Mg,Fe)₂SiO₄, with the end-members now given mineral names to become the ringwoodite–ahrensite solid solution, along with majoritic garnet and MgSiO₃ ilmenite, akimotoite (Agee, 1998; Gasparik, 1990). Both MgSiO₃ ilmenite and garnet contain [6]-coordinated silicon species. Majoritic garnets exist as solid solutions containing

Mg²⁺, Fe²⁺, and Ca²⁺ in the large (8–12 coordinated) site; Al³⁺, Si⁴⁺, and Fe³⁺ in octahedral sites; and Si⁴⁺/Al³⁺ cations on tetrahedral positions.

In the lower mantle, it is established that the primary mineral phase is a silicate perovskite with composition near (Mg_{0.9}Fe_{0.1})SiO₃ that also contains a few percent Al₂O₃ component (Hemley and Cohen, 1992). This coexists with (Mg,Fe)O (magnesiowüstite), which maintains its rock salt (B1) structure throughout the lower mantle (Lin et al., 2003), and also a CaSiO₃ perovskite phase (Hemley and Cohen, 1992). (Mg_{0.9}Fe_{0.1})SiO₃ perovskite then transforms to a CaIrO₃-structured polymorph under pressure and temperature (*P,T*) conditions of the base of the lower mantle (Murakami et al., 2004a; Oganov and Ono, 2004; Tsuchiya et al., 2004c). Stishovite (rutile-structured SiO₂) transforms to CaCl₂- and then α -PbO₂-structured phases below 1250 km (*P* > 50 GPa), *via* displacive phase transitions driven by the vibrational lattice dynamics (Andrault et al., 1998; Dubrovinsky et al., 1997; Kingma et al., 1995; Shieh et al., 2005). Such silica-rich phases could be present in basaltic regions derived from subducted oceanic crust within the lower mantle.

All of these mantle minerals are nominally anhydrous, but they might contain significant quantities of dissolved H as 'defect' OH species (Bell and Rossman, 1992). In addition, various high-pressure hydrous phases, often with compositions expressed in the system MgO–SiO₂–H₂O, could be present especially within the transition zone (Kanzaki, 1991b; Liu, 1987; Prewitt and Finger, 1992). Other studies have focused on the role of hydrous silicate phases, where the H₂O component is present as a molecular component or as an OH group integrated within the mineral structure, as potential water carriers to the transition zone and lower mantle in the relatively cold environment of subduction zones (Komabayashi et al., 2004; Stalder and Ulmer, 2001; Ulmer and Trommsdorff, 1995).

Partial melting occurs within the upper mantle and is likely to occur near the core–mantle boundary (Akins et al., 2004; Hemley and Kubicki, 1991; Shen and Heinz, 1998; Wolf and McMillan, 1995). Early stage scenarios of the Earth's formation involve a deep magma ocean in both the upper mantle and the lower mantle (Labrosse et al., 2007). Understanding the structures and dynamics properties of molten silicates at high pressure is thus important for deep Earth geophysical studies: these have been reviewed previously, and new experimental and theoretical work is appearing in this area (Dingwell, 1998; Jackson et al., 2013; Karki and Stixrude, 2010; Sanloup et al., 2013; Stixrude et al., 2009; Wolf and McMillan, 1995).

Mineral physics involves the application of physics and chemistry techniques to understand and predict the fundamental behavior of Earth materials (Anderson, 1995; Gramaccioli, 2002; Hemley, 1998; Kieffer and Navrotsky, 1985; Navrotsky, 1994) and extend these to large-scale problems in Earth and planetary sciences. Studies of mineral lattice vibrations are central to these studies. Lattice vibrations contribute fundamentally to the thermal free energy of minerals and to the determination their stability. The specific heat is mainly stored and transported *via* vibrational excitations, so that studying mineral lattice dynamics also helps us understand thermal budgets within the mantle (Chai et al., 1996; Hofmeister, 1999; Jeanloz and Morris, 1986; Jeanloz and Richter, 1979; Kieffer, 1979a,b,c, 1980, 1985).

Vibrational modes in solids and liquids are controlled by the same interatomic forces that determine their elastic properties and eventually seismic propagation velocities within the Earth, and they contribute to the fracture kinetics and rheology of mineral assemblages (Amiguet et al., 2012; Bass, 1995; Bina, 1998; Birch, 1952; Brown et al., 1989; Caracas and Gonze, 2010; Carrez and Cordier, 2010; Cordier et al., 2012; Hofmeister, 1991a,b; Liebermann and Li, 1998; Stixrude and Lithgow-Bertelloni, 2005; Weidner, 1975, 1998). Mineral phase transitions can be determined by vibrational excitations as well as by chemical driving forces. The occurrence of lattice dynamics instabilities as a function of *P* and *T* can lead to unexpectedly large changes in mineral elastic properties at depth within the Earth (Caracas, 2005, 2008; Caracas and Gonze, 2010; Iitaka et al., 2004; Kingma et al., 1995; Murakami et al., 2003; Nakagawa and Tackley, 2004; Salje, 1990; Scott, 1974). Consideration of vibrational lattice instabilities of minerals can also allow us to understand and predict melting under high-*P,T* conditions (Akins et al., 2004; Alfé, 2005; Alfé et al., 1999, 2004; Shen and Heinz, 1998; Wolf and Jeanloz, 1984).

Vibrational spectroscopy is used to identify and carry out in situ structural studies of high-pressure mineral phases, including samples contained inside xenoliths and mineral inclusions or within products of high-*P,T* experimental runs. Microbeam Raman and IR spectroscopic techniques have proved highly useful for such studies (Gillet et al., 1998; McMillan, 1985, 1989; McMillan and Hofmeister, 1988; McMillan et al., 1996a,b). Vibrational spectroscopy is particularly useful when applied to highly disordered or amorphous materials, including melts, glasses, and phases containing light-element (C, O, and H) 'volatile' species (Bell and Rossman, 1992; Ihinger et al., 1994; McMillan, 1985, 1989, 1994; McMillan and Wolf, 1995; Rossman, 1996). The optical spectroscopy experiments are enabled with the transparent diamond anvil window in diamond anvil cell (DAC) studies that are used to carry out in situ studies of mineral behavior into the multimegabar range (Challener and Thompson, 1986; Chervin et al., 1992; Ferraro, 1984; Gillet et al., 1998; Hemley, 1998; Hemley and Mao, 2002; Hemley et al., 1987a).

2.09.1.2 Experimental Vibrational Spectroscopy of Mantle Minerals

Many experimental studies of mineral lattice vibrations have been carried out at ambient conditions primarily using Fourier transform IR (FTIR) spectroscopy, typically employing powder transmission methods (Farmer, 1974; McMillan, 1985; McMillan and Hofmeister, 1988). Reflectance IR studies carried out on single crystals or pressed powder samples provide additional information on the lattice dynamics (Gervais, 1983; Gervais and Piriou, 1975; Gervais et al., 1973a; Hofmeister, 1987, 1996, 1997; McMillan, 1985; McMillan and Hofmeister, 1988; Piriou and Cabannes, 1968; Spitzer et al., 1962). In situ FTIR measurements of mantle minerals at high-*P* conditions in the DAC have been carried out (Gillet et al., 1998; Hofmeister, 1996, 1997; Hofmeister and Ito, 1992; Hofmeister et al., 1989; McMillan et al., 1996b; Williams et al., 1986, 1987). IR emission spectroscopy has also been applied during in situ high-*T* studies of minerals and melts; this technique is likewise well adapted for remote-sensing studies of

planetary surfaces and their atmospheres (Christensen et al., 1992; Efimov, 1995; Gervais, 1983; McMillan and Wolf, 1995). Access to synchrotron IR sources allows greatly increased flux for mineral physics studies, especially in the far-IR region (Hemley et al., 1998).

The other main laboratory technique for studying mineral vibrational spectra is Raman spectroscopy that relies on the inelastic scattering of light by vibrational excitations in molecules and solids (Hemley et al., 1987a; Long, 1977; McMillan, 1985, 1989; McMillan and Hofmeister, 1988). The related technique of Brillouin scattering is used to determine the propagation of sound waves within solids at very low energies *via* high-resolution interferometric techniques, and it provides information on the elastic properties of mantle minerals, including under high- P,T conditions (Bass, 1995; Weidner, 1975). Raman and Brillouin spectroscopic studies have been performed up to megabar pressures in the DAC (Murakami et al., 2007; Shim et al., 2007). The IR and Raman spectroscopic studies provide information on vibrational waves propagating inside solids with very long wavelengths (e.g., $\lambda_{\text{vib}} \sim 500$ nm in the case of Raman scattering and $\lambda_{\text{vib}} \sim 1\text{--}50$ μm for IR studies) (Decius and Hexter, 1977; Farmer, 1974; McMillan, 1985; McMillan and Hofmeister, 1988).

In order to study the full lattice dynamics, including the shortest-wavelength lattice modes that exist down to $\lambda_{\text{vib}} \sim a_0$ (i.e., on the order of mineral lattice dimensions), it is necessary to use alternative techniques including INS or IXS. INS studies are implemented at large-scale reactor, or spallation sources appropriate 'cold' neutron beams to probe the vibrational excitations over a wide energy and momentum transfer range (Choudhury et al., 2002; Dove, 2002; Ghose, 1985, 1988; Winkler, 2002). INS experiments typically require large samples and long data collection times, and this has limited their application to complex mineral structures and in situ high- P,T experiments. Several INS studies of important mineral structures, including olivine, pyroxene, and garnet phases relevant to mantle mineralogy, have been carried out on powdered samples to provide data on the vibrational density of states (VDOS, or the $g(v)$ function) that represents the mineral lattice vibrational spectrum averaged over all crystallographic directions (Chaplot et al., 2002; Choudhury et al., 1998, 2002; Mittal et al., 2000; Price et al., 1991; Rao et al., 1988, 1999, 2002). When large single crystals are available, INS measurements reveal the expected dependence of vibrational energies on the wavevector for phonon propagation along different crystallographic directions in reciprocal space. Such studies have so far been restricted to lower crustal and upper mantle minerals, as well as diamond and periclase, the rock salt-structured MgO (Bilz and Kress, 1979; Chaplot et al., 2002; Choudhury et al., 2002; Dove, 1993).

In situ neutron studies of materials under high- P,T conditions have been enabled by coupling neutron scattering techniques with high-pressure devices, including the versatile 'Paris-Edinburgh' press design (Besson et al., 1992; Dove, 2002; Khvostantsev et al., 2004; Loveday, 2004; Redfern, 2002). The lattice dynamics of Ge and *bcc*-Fe have been determined up to $P \sim 10$ GPa (Klotz and Braden, 2000; Klotz et al., 1997). Neutron diffraction studies can now be carried out to $P \sim 30$ GPa at low T and up to $P \sim 10$ GPa under simultaneous high- P,T conditions (Loveday, 2004; Redfern, 2002). Those

limits are now being extended into the multi-GPa or megabar regime using new cell designs and materials combined with advanced neutron focusing and detector techniques (Bull et al., 2005; Irifune, 2002; Loveday, 2004).

New experimental approaches for determining mineral lattice dynamics under high- P,T conditions have also been developed at synchrotron facilities, using techniques including high-resolution IXS and nuclear resonant spectroscopies at synchrotron facilities (Duffy, 2005; Fiquet et al., 2001; Hemley and Mao, 2002; Kao et al., 1996; Mao et al., 2001; Schwoerer-Böhning et al., 1998; Zhao et al., 2004). These techniques are well adapted to multimegabar DAC investigations, extending to high T , using focused x-ray beams. The nuclear resonant techniques are specific to Mössbauer absorbing atoms with appropriate γ -ray resonances, of which iron is the most relevant for geophysics with Fe-based alloys present or prevalent throughout the Earth's mantle and core (Mao et al., 2001, 2005; Zhao et al., 2004). These techniques provide phonon density-of-states and dispersion data that are complementary to INS studies (Antonangeli et al., 2011; Duffy, 2005; Fiquet et al., 2001; Hemley and Mao, 2002; Lin et al., 2005; Mao et al., 2001; Zhao et al., 2004).

2.09.1.3 Mineral Lattice Dynamics Calculations

Vibrational spectroscopy experiments are complemented and extended by theoretical calculations of mineral lattice dynamics under high- P,T conditions. A wide range of empirical and semiempirical methods based on the ionic model were first developed to predict and understand the energetics, structures, lattice dynamics, and thermoelastic properties of mantle minerals under high- P,T conditions (Burnham, 1985, 1990; Catlow and Price, 1990; Dove, 1993; Matsui, 1988; Matsui and Busing, 1984; Matsui et al., 1987; Price et al., 1987; Tse, 2004; Winkler, 2004). By the mid-1980s, *ab initio* calculations in molecular chemistry established using Hartree-Fock techniques (Hehre et al., 1996) were applied to silicate clusters that are important for mineralogy studies (Gibbs, 1982; Sauer, 1989; Toscell and Vaughan, 1992). First and second derivatives of the energy with respect to atomic displacements give *ab initio* force constants for lattice dynamics calculations and were used to construct potential functions for molecular and lattice dynamics simulations (Caracas et al., 2010; Gonze et al., 2005; Hess et al., 1986; Lasaga and Gibbs, 1987; McMillan and Hess, 1990; Tsuneyuki et al., 1988; van Beest et al., 1994). In an alternative approach, the lattice dynamics of important mantle minerals were modeled using modified electron gas theory (Chizmeshya et al., 1994; Cohen, 1987; Cohen et al., 1987a,b; Hemley and Cohen, 1992; Hemley and Gordon, 1985; Hemley et al., 1987b; Ita and Cohen, 1998; Mehl et al., 1986; Wolf and Bukowinski, 1987; Wolf and Jeanloz, 1985).

Following continued progress in computational methods combined with the dramatic increase in computer capacity and performance, *ab initio* or 'first principles' calculations of mineral lattice dynamics are now performed accurately into the highest P,T ranges, where experimental vibrational spectroscopic data may not be available and may not be obtainable using current technologies (Bukowinski, 1994; Caracas, 2008; Caracas and Cohen, 2006; Caracas et al., 2010; Jung and Oganov, 2005; Karki et al., 2001; Oganov, 2004; Oganov et al., 2002, 2005; Stixrude and Lithgow-Bertelloni, 2005;

Stixrude et al., 1996, 1998; Tsuchiya and Tsuchiya, 2011; Wentzcovich et al., 2004a). New experimental results must continue to be obtained to calibrate and complement the theoretical calculations, however. One fundamental issue concerns the anharmonic vibrational properties of minerals that are not yet fully accounted for theoretically, so that the predicted behavior at high T and high P must be tested by experiments whenever possible (Baroni et al., 2001; Caracas and Boffa-Ballaran, 2010; Gonze et al., 2005). Further advances in mineral physics studies thus require continued close interaction between theoretical and experimental studies, as we investigate and determine the behavior of materials that occur deep within the Earth and extend the work to other planetary systems in this solar system and beyond.

2.09.2 Mineral Lattice Dynamics and Vibrational Spectroscopy

2.09.2.1 Theoretical Basis for the Treatment of Lattice Vibrations

The atomic arrangement of molecules and crystalline structures is not rigid as suggested by crystallography and classical models of structure. The atoms must always be in motion about their 'equilibrium positions' even at $T=0$ K as determined by quantum mechanics. That gives rise to the phenomenon of 'zero-point vibrational energy' that exists at all temperatures and contributes to the crystalline free energy at all temperatures. However, we can leave aside consideration of this fact as we develop the classical variation in total energy (E) as a function of small atomic displacements (τ) about their equilibrium positions, expanded in a Taylor series (Figure 1):

$$E(\tau) = E^0(\tau) + \sum_{i,\alpha} \left(\frac{\partial E}{\partial \tau_{i,\alpha}} \right) d\tau_{i,\alpha} + \sum_{i,j,\alpha,\beta} \left(\frac{\partial^2 E}{\partial \tau_{i,\alpha} \partial \tau_{j,\beta}} \right) d\tau_{i,\alpha} d\tau_{j,\beta} + \sum_{i,j,k,\alpha,\beta,\gamma} \left(\frac{\partial^3 E}{\partial \tau_{i,\alpha} \partial \tau_{j,\beta} \partial \tau_{k,\gamma}} \right) d\tau_{i,\alpha} d\tau_{j,\beta} d\tau_{k,\gamma} + \dots \quad [1]$$

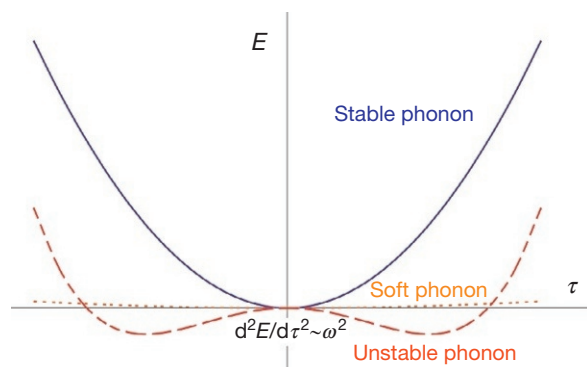


Figure 1 Lattice energy E as a function of perturbation in atomic position τ . At equilibrium position, $\tau=0$, the energy is minimum. The phonon frequency ω is determined by the curvature of the energy curve around the equilibrium position (blue curve). The frequency of a soft phonon (orange curve) goes to zero as a second order is approached. The frequency becomes imaginary if the phonon is unstable, and the lattice distorts to reach positions corresponding to the new energy minima (red curve).

Here, the subscripts, $i, j, k, \dots$ denote atoms in the $\alpha, \beta, \gamma, \dots$ crystalline unit cells, as they are displaced along each of the three Cartesian directions. The first term in the expansion (E^0) is the ground-state energy, given by the macroscopic heat of formation from the elements or by the ground-state Born–Oppenheimer energy determined in a static first principles calculation. The second term is the first derivative of the energy with respect to atomic displacements, $\partial E / \partial \tau$, which yields the forces acting upon the atoms. This is identically zero for a structure at mechanical and thermodynamic equilibrium, but that comes into play when the crystal is placed under an unbalanced external stress. The third term is the second derivative of the energy, $\partial^2 E / \partial \tau_{i,\alpha} \partial \tau_{j,\beta}$, which corresponds to the interatomic force constants, $k_{i,j}$, of the mineral or compound treated as a collection of harmonic oscillators. Here, the atoms are presumed to oscillate around their equilibrium positions in patterns determined by the crystal symmetry, and coupling between the motions in different unit cells leads to the concept of lattice vibrations. Any third-order derivatives or higher-order terms included in the expansion participate in an anharmonic description of the vibrations. The truncation of the Taylor series (eqn [1]) after the second-order derivative constitutes a 'quasiharmonic' (QH) approximation of the vibrational properties of the system. This approximation is currently employed within density-functional perturbation theory (DFPT) approaches (Baroni et al., 2001). However, its current formulation contains drawbacks that lead to discrepancies occurring between computed and measured vibrational properties that must be addressed in future implementation of their approach.

We can analyze in detail the second-order derivatives of the energy that are employed in the ideal description of a structure with elastic-type-only interatomic forces. The interatomic force constants form a tensor with dimensions $3n \times 3n$, where the factor 3 comes from the three Cartesian directions and n is the total number of atoms in the crystal, typically on the order of 10^{23} – 10^{25} if one or several moles of materials are present. Determining such a large matrix is obviously intractable, but we can make use of the translational symmetry of the crystalline lattice to reduce it to a series of equivalent matrices that describe the interactions between the atoms belonging to pairs of unit cells, separated by a distance λ that corresponds the lattice dimension. These new matrices characterized by λ have dimension $3N \times 3N$, where N is the number of atoms in the unit cell. Following normalization by the atomic masses and Fourier transformation into reciprocal space, they result in the dynamics matrices for the system. These are defined for a particular $\mathbf{q}$ vector, which describes the distance between families of pairs of cells as well as the phase relationships of their vibrational oscillations. Its norm is $\mathbf{q} = 2\pi/\lambda$, with $\mathbf{q}$ defined in the reciprocal space and λ in the direct space.

The diagonalization of the dynamics matrices yields all the necessary information about the atomic vibrations. The eigenvalues give the square of all the vibrational frequencies $\omega_i(\mathbf{q})$, and the corresponding eigenvectors give the atomic displacement pattern of each mode, where i is the index of the vibration and its values go from 1 to $3N$. As for finite molecules, there is a direct relation between the curvature of the energy around the atomic equilibrium positions (Figure 1) and the vibrational frequency. We note that three of the values do not correspond to true vibrations but to Cartesian

displacements of the entire crystal. A further three solutions should also correspond to rotational degrees of freedom of the object, but these are usually only considered explicitly in treatments of finite molecules rather than crystalline solids.

If the second energy derivative is positive for all vibrations and all $\mathbf{q}$ vectors, all vibrational frequencies correspond to real solutions and the structure is dynamically stable. When one or more of the second-order energy derivatives are negative for a given $\mathbf{q}$ vector (Figure 1), the corresponding dynamics matrix will yield at least one imaginary frequency $\omega_i(\mathbf{q})$. Such a solution does not correspond to an oscillatory solution but to a displacement of the atoms along the indicated eigenvector. In this case, the crystal structure is unstable, as at least one collective atomic displacement will lower the energy of the structure. The result is a permanent distortion of the structure away from the initial configuration, and the result is a displacive structural transformation that may correspond to a second-order phase transition if only a single vibrational mode is concerned or to a first-order transition if several are implicated in the phenomenon.

In the case where a single vibrational mode becomes unstable, the frequency is observed to decrease asymptotically to zero in a second-order phase transition, giving rise to 'soft-mode' behavior (Baroni et al., 2001; Caracas and Boffa-Ballaran, 2010; Dove, 1993; Gonze et al., 2005). The phenomenon was first observed for quartz, in which the α - β transition at 858 K is associated with a vibrational mode occurring at $\sim 207\text{ cm}^{-1}$ at ambient T and P (Raman and Nedungadi, 1940; Scott, 1974). The mode eigenvector corresponds to the set of atomic displacements linking the two structures, and the point at which the vibrational frequency vanishes determines the phase transition. Soft-mode behavior has been predicted and observed for important mantle minerals including CaSiO_3 perovskite, in which a cubic-tetragonal transition occurs, and SiO_2 stishovite, where it leads to a transformation into a CaCl_2 -structured phase (Andrault et al., 1998; Caracas, 2005; Caracas and Cohen, 2006; Chizmeshya et al., 1996; Cohen, 1992; Hemley and Cohen, 1992; Kingma et al., 1995; Stixrude et al., 1996).

The most accurate methods today use *ab initio* descriptions of the lattice energy using density-functional theory (DFT) (Hohenberg and Kohn, 1964; Kohn and Sham, 1965; Payne et al., 1992). When the Taylor expansion of the energy is considered within DFT, the method is known as density-functional perturbation theory (Baroni et al., 1987, 2001; Gonze and Lee, 1997; Gonze and Vigneron, 1989; Gonze et al., 2005). The computational cost is comparable with that of static DFT calculations. A fully *ab initio*/first principles treatment including intrinsic anharmonic effects can also be achieved using quantum molecular dynamics or quantum Monte Carlo methods (Alfé et al., 1999; Ancilotto et al., 1997; Car and Parrinello, 1985; Cavazzoni et al., 1999; Remler and Madden, 1990). The Taylor expansion can also be realized in terms of other lattice 'perturbations,' including atomic displacements resulting from electronic charge or spin redistribution in response to applied electric or magnetic fields or mechanically induced strain, and these effects that can be coupled together are also important in mineral physics investigations (Baroni et al., 2001; Hamann et al., 2005).

One particularly important application is the calculation of the elastic constants tensors associated with mechanical

deformation. This was historically done using linear stress-strain relations, and with the residual stresses computed directly onto deformed lattices, the calculation of the elastic constants can now be achieved directly using DFPT methods. In this case, the energy expansion is written in terms of strains, which induce atomic displacement and electric fields. The theoretical basis of this development was proposed some time ago (Baroni et al., 1987), but only recently, the description of the derivatives using the crystallographic reference frame (Hamann et al., 2005) has allowed application of the methodology for practical calculations on mantle minerals (Caracas and Boffa-Ballaran, 2010; Caracas et al., 2010).

2.09.2.2 Vibrational Dispersion Relations and Phonons

Vibrational modes in crystalline solids are readily described as planar waves of atomic displacement traveling throughout the solid. The corresponding quantized units of vibrational excitation are termed *phonons*, by analogy with the definition of *photons* for light 'particles' (Dove, 1993). The quantity $\hbar q$ associated with each phonon has units of momentum (i.e., kg m s^{-1}), so that phonons possess an 'effective' mass and thus behave as 'quasiparticles.' Transverse (T) and longitudinal (L) modes are distinguished by the orientation of atomic displacement vectors relative to the propagation direction; transverse lattice modes have a vibrational oscillation of atoms about their equilibrium position that is generally normal to the direction of propagation. They are characterized by their wavevector, which corresponds to $\mathbf{q}$ from the earlier mentioned definition of the dynamics matrices. The $\mathbf{q}$ vectors are described in the reciprocal space; their position is usually restricted to the first Brillouin zone – the smallest region of space defined by the Bragg planes around each integer point of the reciprocal lattice. Transfer of vibrational energy into higher Brillouin zones is important for transport of vibrational thermal energy throughout the crystal and appears in discussions of thermal conductivity (Hofmeister, 1999). Resulting from the diagonalization of the dynamics matrices, there are $3N$ vibrational 'modes' for each $\mathbf{q}$ vector. Usually, the vibrational frequencies are shown along a given high-symmetry path within the Brillouin zone (Bilz and Kress, 1979; Choudhury et al., 2002; Dove, 1993; McMillan, 1985). This representation yields the phonon dispersion relations, as shown for diamond in Figure 2.

The $\mathbf{q}=0$ point occurs at the Brillouin zone center, termed the Γ point. The vibrations whose wavevector is at Γ in the reciprocal space have the same phase and amplitude in every unit cell of the crystal lattice, because their wavevector in the direct space is infinite, $\lambda = 2\pi/0 = \infty$. Three of the phonons at Γ stem from the displacement of all atoms with the same amount along each of the three Cartesian direction; hence, they have null frequency: these constitute the *acoustic* modes whose initial dispersion relations at long wavelength determine the sound speeds in the material (Bass, 1995; Hamann et al., 2005; Kieffer, 1979a,b,c; Liebermann and Li, 1998; Weidner, 1975, 1987). The remaining $3N-3$ branches are the *optic* branches that can lead to IR and Raman activities. Only vibrational excitations with $\mathbf{q}\sim 0$ can usually be observed in IR or Raman spectra, due to the long-wavelength nature of the incident light waves (McMillan, 1985; McMillan and Hofmeister, 1988). However, all of the modes can interact with and be probed by 'slow' neutrons (i.e., neutron beams thermally

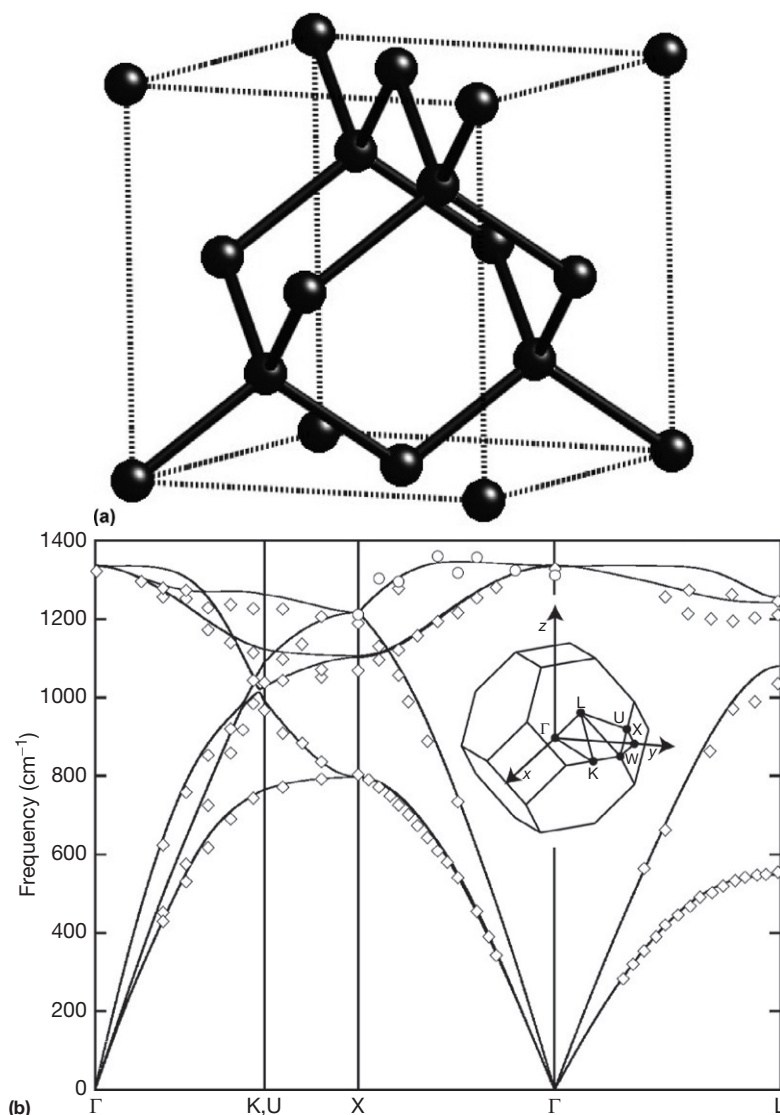


Figure 2 Structure and lattice vibrations of diamond. (a) The cubic diamond structure contains two atoms in its primitive unit cell. (b) The lattice dynamics of a single crystal of diamond computed along various directions of the reciprocal space using DFT (thin curves) are compared with inelastic neutron and x-ray scattering data (symbols) (Gonze et al., 2005). Three acoustic modes rise from zero frequency (two TA + one LA modes); these determine the sound speed and the elastic properties and the thermal conductivity. Three additional modes constitute the optic branches (two TO + one LO) that converge to provide the single Raman-active frequency (T_{2g} symmetry) at the Brillouin zone center. The diagrams in (b) are reprinted from Gonze X, Rignanese GM, and Caracas R (2005) First-principles studies of the lattice dynamics of crystals, and related properties. *Zeitschrift für Kristallographie* 220: 458–472, with permission. Edition copyright, © 2005 Oldenbourg Wissenschaftsverlag GmbH.

equilibrated near $T=300$ K) in INS experiments, to provide a complete picture of the lattice dynamics (Bilz and Kress, 1979; Chaplot et al., 2002; Choudhury et al., 2002; Dove, 1993; Ghose, 1988; Winkler, 2002). IXS experiments developed at synchrotron sources now also permit observation of the energy transfer over a wide $\mathbf{q}$ range, and these are likewise used to probe the phonon dispersion relations (Mohr et al., 2007; Sette et al., 1998). The advantage in this case is that measurements can readily be carried out in the DAC to extremely high pressures and also at variable temperature (Antonangeli et al., 2011; Fiquet et al., 2001, 2004).

As any physical property of the crystals, the phonons obey the symmetry of the lattice. The response of the phonons in

one particular $\mathbf{q}$ point to the point group symmetry is classified based on the irreducible representations and defines their character (Bradley and Cracknell, 1972; Decius and Hexter, 1977; Maradudin et al., 1963; Srivastava, 1990). The vibrations at Γ are typically given symmetry labels according to their character and degeneracy (e.g., A_1 , B_{2g} , E_g , and T_{1u}) like the vibrational modes discussed in molecular chemistry and determined by group theory/symmetry analysis. The group theoretical approach also allows prediction of the IR and Raman activities of the vibrational modes (Cotton, 1971; Decius and Hexter, 1977; Fateley et al., 1972; Hamermesh, 1962; McMillan, 1985; McMillan and Hofmeister, 1988; Schrader, 1994).

2.09.2.3 Beyond the QH Approximation

The quasiparticle nature of phonons gives rise to the inelastic scattering phenomena observed to occur with neutrons in INS experiments and with photons in Raman, Brillouin, and inelastic XRS spectroscopies. The phonon ‘quasiparticles’ can also scatter among themselves; this results in features of vibrational *anharmonicity*, which we develop and discuss later. These processes are temperature-dependent, and phonon–phonon interactions are likely to play a key role in determining the high-temperature properties of mantle minerals (Gillet et al., 1991, 1996a, 1997, 1998, 2000b; Oganov et al., 2000; Reissland, 1973; Wallace, 1972; Wentzcovich et al., 2004a,b; Wolf and Jeanloz, 1984).

In the previous discussion, the harmonic Taylor expansion of the energy was truncated after the second-derivative term. However, this approximation based on a symmetric parabolic behavior of the energy only holds for infinitesimal displacements. Realistic *potential energy* curves determined for diatomic molecules deviate significantly from this relation and are thus *anharmonic* (Herzberg, 1945, 1950; McMillan, 1985; McMillan and Hofmeister, 1988; Nakamoto, 1978). Adding higher-order terms in the Taylor expansion helps reproduce this behavior within a classical model. The inclusion of such terms into computational studies allows the calculation of important *non-linear* physical properties including the Raman tensors and other nonlinear optical coefficients (Baroni and Resta, 1986; Lazzeri and Mauri, 2003; Veithen et al., 2005).

The interactions between phonons, with either the same or different $\mathbf{q}$ vectors, can only be correctly described by considering the higher-order derivatives of the energy with respect to atomic displacement parameters. These interactions influence a wide series of phenomena related to lattice heat transport and other thermodynamic functions, as well as phonon bandwidths and the appearance of Raman and IR peaks due to ‘overtone’ and ‘combination’ modes of vibration. These typically have much weaker intensity than ‘fundamental’ transitions that occur between the vibrational ground state (i.e., all $n_i=0$) and the first excited state for each vibration and can be useful in determining the potential energy surface for molecules and crystals (Decius and Hexter, 1977; Herzberg, 1945), as well as constraining the anharmonicity of O–H bonds important for water transport in mantle minerals (Balan et al., 2007; Reynard and Caracas, 2009).

Most first principles calculations of mantle minerals do not evaluate the effects of intrinsic phonon anharmonicity explicitly but rely on a QH model that can successfully reproduce many of the thermoelastic properties under the range of high- P,T conditions encountered within the lower mantle and transition zone (Gillet et al., 2000b; Guyot et al., 1996; Hamann et al., 2005; Karki and Wentzcovich, 2002; Wentzcovich et al., 2004b). However, some phase equilibrium calculations for phase transitions involving major structural transformations, such as that between MgSiO_3 ilmenite and perovskite, have shown significant differences from the experimental P,T transition line that could be assigned to intrinsic anharmonic phonon effects (Wentzcovich et al., 2004b).

2.09.2.4 Raman Tensors

One particular application of the higher-order derivative terms is the theoretical determination of the intensity of

Raman-active vibrations of minerals. A full perturbation expansion to the third order, expressed in terms of electric fields, ε , and atomic displacements, τ , derived from eqn [1] is

$$\begin{aligned}
 F_{e+i}[R_k, E] = & F_{e+i}[R_k, E] \\
 & - \Omega_0 \sum_{\alpha} P_{\alpha}^s \varepsilon_{\alpha} - \sum_{\alpha} \sum_k F_{\alpha}^0 \tau_{k\alpha} \\
 & - \Omega_0 / 2 \sum_{\alpha\beta} \chi_{\alpha\beta}^{\infty(1)} \varepsilon_{\alpha} \varepsilon_{\beta} - \sum_{\alpha\beta} \sum_{\kappa} Z_{\kappa, \alpha\beta}^* \tau_{\kappa\alpha} \varepsilon_{\beta} \\
 & + 1/2 \sum_{\alpha\beta} \sum_{\kappa\kappa'} C_{\alpha\beta}(\kappa, \kappa') \tau_{\kappa\alpha} \tau_{\kappa'\beta} \\
 & - \Omega_0 / 3 \sum_{\alpha\beta\gamma} \chi_{\alpha\beta\gamma}^{\infty(2)} \varepsilon_{\alpha} \varepsilon_{\beta} \varepsilon_{\gamma} \\
 & - \Omega_0 / 2 \sum_{\kappa} \sum_{\alpha\beta} \frac{\partial \chi_{\alpha\beta}^{\infty(1)}}{\partial \tau_{\kappa\gamma}} \varepsilon_{\alpha} \varepsilon_{\beta} \tau_{\kappa\gamma} \quad [2] \\
 & \text{Raman coeff.}
 \end{aligned}$$

Important physical properties including electric polarization and dielectric tensors or dynamics charges (amount of electronic charge exchanged by two bonded atoms during vibration) can be extracted from this expression (Veithen et al., 2005). The coefficients determining Raman activity represent the mixed derivative of the energy with respect to the incident and scattered electric fields and the atomic displacement coordinates. In other words, they express how the dielectric tensor, the second-order derivative of the energy with respect to two electric fields or electric field components, changes during the atomic displacements associated with a vibrational mode and determines the intensity of the Raman peaks, I_{xy} :

$$I_{xy} \approx \frac{(\omega_L - \omega_i)^4}{c^4} \alpha_{xy}^2 \frac{(1 + n(\omega_i))}{30\omega_i} \quad [3]$$

where

$$\alpha_{xy} = \sqrt{\Omega_0} \quad [4]$$

and

$$1 + n(\omega_i) = [1 - \exp(-\hbar\omega_i/2\pi kT)]^{-1} \quad [5]$$

is the Bose occupation factor (Bose, 1924).

The computation of the Raman tensors α_{xy} can be achieved using a ‘frozen-phonon’ approach where the atoms are displaced by hand and the dielectric tensors computed at every step or by using a direct application of the DFPT up to third order. The latter approach is now available in several computational packages: for example, Quantum ESPRESSO (Lazzeri and Mauri, 2003), ABINIT (Veithen et al., 2005), and CASTEP (Clark et al., 2005). It has been extensively used in theoretical studies of mantle minerals at high pressure (Caracas and Banigan, 2009; Caracas and Cohen, 2006, 2007b; Lazzeri and Mauri, 2003). The ABINIT implementation provides the computational basis of the WURM project (Caracas and Bobocioiu, 2011) that is currently building a database of computed physical properties for minerals from DFPT calculations. The focus of the database is on the Raman spectra of minerals, with both peak positions and peak intensities reported.

2.09.2.5 Vibrational Frequency Shifts at High P and T : QH Model and Phonon Anharmonicity

Within crystals, the anharmonic nature of the interatomic potential generally causes the interatomic distances (r) to shift to larger values as T is increased, resulting in thermal expansion. Vibrational frequencies typically shift to lower wave number with increasing T , and they increase with P , due to the asymmetric form of the interatomic potential energy function (Herzberg, 1950; McMillan, 1985). Within the QH model of mineral lattice dynamics, the lattice expands or contracts according to the high- P , T conditions, and a new set of harmonic phonons is considered to exist at each new set of distances and interatomic configurations. No phonon-phonon scattering events are considered to occur, and the vibrational linewidths measured in IR, Raman, or INS spectroscopy are predicted to be independent of temperature.

The vibrational frequency shifts as a function of P or T (i.e., $(\partial v_i/\partial P)_T$ and $(\partial v_i/\partial T)_P$) are expressed in terms of volume (V) as mode Grüneisen parameters: that is,

$$\gamma_i = \frac{d \ln v_i}{dV} \quad [6]$$

For data measured at constant T and variable P , these parameters are obtained by

$$\gamma_{iT} = \frac{K_T}{v_i} \left(\frac{\partial v_i}{\partial P} \right)_T = K_T \left(\frac{\partial \ln v_i}{\partial P} \right)_T \quad [7]$$

where K_T is the isothermal bulk modulus. For data determined at variable T and constant P , the corresponding parameters are obtained using the volume thermal expansion coefficient (α):

$$\gamma_{iP} = -\frac{1}{\alpha v_i} \left(\frac{\partial v_i}{\partial T} \right)_P = -\frac{1}{\alpha} \left(\frac{\partial \ln v_i}{\partial T} \right)_P \quad [8]$$

Measured mode Grüneisen parameters are averaged to give an approximate mean value ($\langle \gamma \rangle$) that can be compared with the 'thermal' Grüneisen parameter (γ_{th}) that appears in mineral equation of state formulations (Anderson, 1995; Duffy and Wang, 1998; Gillet et al., 1998; Holzapfel, 2004; Jeanloz, 1985):

$$\gamma_{th} = \frac{\alpha K_T V}{C_v} \quad [9]$$

Conversion of observed $v_{iT}(P)$ and $v_{iP}(T)$ data into $v_i(V)$ relations using measured values for the bulk modulus and the thermal expansion coefficient, respectively, provides an experimental test of the QH model. If this approximation held true, both data sets should be colinear. This is *not* found to be the case for the vibrational modes of mantle minerals examined to date (Gillet et al., 1990, 1991, 1993, 1996a, 1997, 1998, 2000b; Reynard and Rubie, 1996; Reynard et al., 1992; Figure 3). The general conclusion is that most vibrational modes for most minerals exhibit some degree of anharmonicity that may affect phase relations and thermophysical properties under high- P , T conditions.

The intrinsic mode anharmonicity represents a dependence of the vibrational frequencies on T at constant volume that arises due to T -dependent phonon-phonon scattering events. The intrinsic mode anharmonicity parameters obtained from the comparison of experimental data for $v_{iT}(P)$ and $v_{iP}(T)$ are expressed as (Gillet et al., 1991, 1997, 1998)

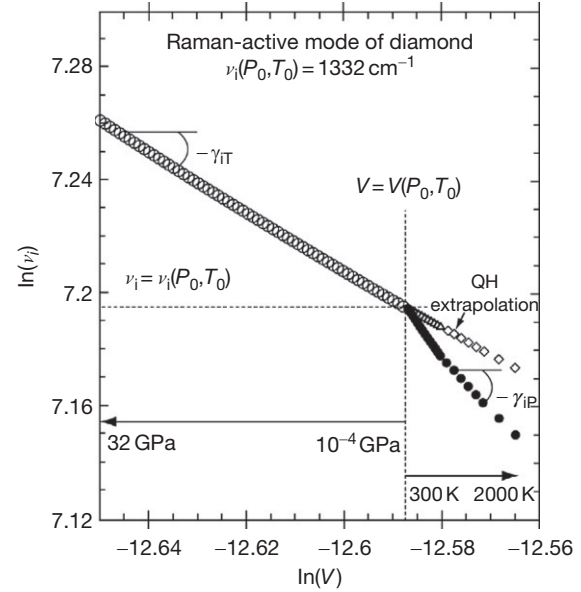


Figure 3 Anharmonicity of the Raman-active mode of diamond, from high- T , ambient P measurements and high- P , ambient T measurements (Gillet et al., 1998). Here, the results from high- P , ambient T , and variable T , $P=1$ atm experiments are combined. The P , T dependencies of the Raman-active mode at the Brillouin zone center ($\Gamma_{vib} = T_{2g}$), that is, $(\partial v_i/\partial P)_T$ and $(\partial v_i/\partial T)_P$, are transformed into volume dependencies using the bulk modulus and thermal expansion coefficients. The two $\partial v_i/\partial V$ relationships should be colinear within a QH model. The observed mismatch between the high-/low- T and the high- P relationships demonstrates that intrinsic phonon anharmonicity is present, and this must be considered in the evaluation of the lattice dynamics and thermophysical properties. Reprinted from Gillet P, Hemley RJ, and McMillan PF (1998) In: Hemley RJ (ed.) *Ultrahigh-Pressure Mineralogy. Reviews in Mineralogy*, Vol. 37. Washington, DC: Mineralogical Society of America, with permission. Copyright (1998) by the Mineralogical Society of America.

$$a_i = \left(\frac{\partial \ln v_i}{\partial T} \right)_V = \alpha (\gamma_{iT} - \gamma_{iP}) \quad [10]$$

The a_i parameters have units K^{-1} . Intrinsic vibrational mode anharmonicities are also obtained from the analysis of IR reflectance data *via* damped oscillator models, in which an anharmonicity parameter (Γ_i) is adjusted to fit the observed reflectivity line shape of each mode (Gervais, 1983; Gervais and Piriou, 1975; Gervais et al., 1973a,b; Hofmeister, 1987, 1997; McMillan, 1985; McMillan and Hofmeister, 1988; Piriou and Cabannes, 1968). Here, the Γ_i parameter represents the width at half maximum of the peak in the dielectric loss function (i.e., $\epsilon_2(v_i)$) associated with IR absorption, and it is a measure of the phonon lifetime (i.e., it has a unit of s^{-1}). The damping Γ_i parameters are also obtained from linewidth measurements of Raman lines at high T and from ab initio DFT calculations, as has been applied to characterize the vibrational anharmonicity in graphite (Bonini et al., 2007; Giura et al., 2012; Lazzeri et al., 2006; Montagnac et al., 2013).

2.09.2.6 Mineral Thermodynamic Quantities from Vibrational Spectra

Within the harmonic model, the vibrational contribution to the Helmholtz free energy (F) at constant V and variable T is

$$F_{\text{th}} = \int_0^{v_{\text{max}}} \frac{h\nu_i}{2} + kT \ln \left(1 - e^{-(h\nu_i/kT)} \right) g(\nu_i) d\nu \quad [11]$$

where the integration runs over the VDOS ($g(\nu)$) to the maximum frequency ν_{max} . Experimental or theoretical determinations of $g(\nu)$ thus lead to prediction and rationalization of important thermodynamic quantities derived from F_{th} , including the heat capacity (C_v or C_p), the 'third law' or vibrational entropy (S_{vib}), and the thermal pressure (P_{th}), using the methods of statistical thermodynamics (Chopelas, 1991; Chopelas et al., 1994; Fiquet et al., 1992; Gillet et al., 1991, 1997, 1998, 2000b; Guyot et al., 1996; Hofmeister, 1996; Hofmeister and Ito, 1992; Hofmeister et al., 1989; Kieffer, 1979a,b,c, 1985; Wallace, 1972).

The contribution of a given vibrational mode ($\nu_i(\mathbf{q})$) to the specific heat at constant volume (C_{Vi}) is

$$C_{Vi} = T \left. \frac{\partial S_i}{\partial T} \right|_V \quad [12]$$

where the vibrational entropy is obtained by integration over $g(\nu)$ of the expression

$$S_i(V, T) = k_B \left[-\ln \left(1 - \exp \left(-\frac{h\nu_i}{k_B T} \right) \right) + \frac{h\nu_i}{k_B T} \frac{1}{\left(\exp \left(\frac{h\nu_i}{k_B T} \right) - 1 \right)} \right] \quad [13]$$

The contribution to the thermal pressure (P_{th}^i) is determined by

$$P_{\text{th}}^i(V, T) - P_{\text{th}}^i(V, T_0) = \int_{T_0}^T \left. \frac{\partial S_i}{\partial V} \right|_{T'} dT' \quad [14]$$

with

$$\left. \frac{\partial S_i}{\partial V} \right|_T = k_B \frac{\gamma_{iT}}{V} \left(\frac{h\nu}{k_B T} \right)^2 \frac{\exp \left(\frac{h\nu}{k_B T} \right)}{\left(\exp \left(\frac{h\nu}{k_B T} \right) - 1 \right)^2} \quad [15]$$

Within the QH model of mineral lattice vibrations, the specific heat at constant pressure (C_p) is related to that at constant volume by

$$C_p = C_v + \alpha^2 V K_T T \quad [16]$$

where α is the coefficient of volume thermal expansion.

Following the approach described by Kieffer (1979a,b,c, 1980, 1985), VDOS models for mantle minerals have been constructed from the experimental vibrational spectra combined with elastic data, and these have been used to predict the thermoelastic properties of important mantle minerals and their phase transitions (Akaogi et al., 1984, 1989; Chopelas, 1990, 1991; Chopelas et al., 1994; Gillet et al., 1991, 1996b, 1997, 2000b; Hofmeister, 1996; Hofmeister and Chopelas, 1991a; Lu et al., 1994). Empirical $g(\nu)$ functions have also been used to calculate mantle mineral thermal conductivity (Hofmeister, 1999). VDOS functions determined experimentally by INS techniques have also been used to calculate C_v and S directly (Chaplot et al., 2002; Choudhury et al., 1998, 2002; Ghose, 1985, 1988; Mittal et al., 2000; Price et al., 1991). Similar studies have been carried out for Fe under deep mantle and core conditions, using $g(\nu)$ functions determined from inelastic XRS techniques (Mao et al., 2001, 2005; Zhao et al., 2004). There

are still no experimental data on the VDOS functions of important mantle mineral phases such as MgSiO_3 perovskite, ilmenite, and garnet, or β - and γ - Mg_2SiO_4 , at ambient or under mantle high- P,T conditions. That information is currently obtained from ab initio or first principles theoretical calculations of the lattice dynamics, usually within the context of the QH model (Chizmeshya et al., 1996; Karki and Wentzcovich, 2002; Karki et al., 2000a,b; Oganov et al., 2002, 2005; Stixrude et al., 1996; Wentzcovich et al., 1993, 2004a). Finally, because vibrational frequencies depend on atomic mass, isotopic fractionation can be modeled using experimental or computed vibrational frequencies and densities of state of isotopic species (Bigeleisen and Mayer, 1947; Schauble, 2004; Urey, 1947).

2.09.2.7 Theoretical Calculations of Mantle Mineral Lattice Vibrations

Following the theoretical approaches described in Section 2.09.1.3, DFT (Hohenberg and Kohn, 1964; Kohn and Sham, 1965; Payne et al., 1992) has become the standard method implemented with first principles methods for theoretical prediction of mineral physical properties applied to geophysics. The Kohn–Sham equations introduced in the original papers represent a singular mapping of the many-body Schrödinger equations on to a functional (i.e., *via* functions of a function) description of the electron density, ρ . The solution of the functional is to be found based on analytical formulations for the electron kinetic energy and for the electrostatic-type energy terms in the single-electron approximation. The multi-body aspects of the approach are hidden in the electronic exchange and correlation term that is not known explicitly but must be modeled. The formalism for this term is known exactly only for a homogeneous electron gas (Perdew and Wang, 1992). Certain difficulties arise in determining the proper exchange–correlation functions for 'real' molecules and solids, including minerals, in which large fluctuations in the electron density (ρ) occur in the vicinity of atomic cores (Perdew et al., 1996).

The electron gas exchange–correlation functions are usually applied to molecules and solids within the local density approximation (LDA), in which a spatially averaged electron density is considered to exist throughout the system. Although it obviously does not account for the large fluctuations in electron density that occur close to the atomic nuclei, the LDA approach has been remarkably successful in describing most of the important structural and thermodynamic properties of minerals and molecules and their chemical bonding (Payne et al., 1992). This arises mainly because most of these properties are largely independent of the electron density fluctuations occurring within the region of the atomic cores. The vibrational frequencies of minerals are usually predicted using DFT–LDA methods to within a few percent (i.e., 5–15%) of experimental values (Baroni et al., 2001; Caracas and Bobocioiu, 2011; Caracas and Gonze, 2010; Gonze et al., 2005). Various 'generalized gradient approximations' (GGA) have been developed to better describe local fluctuations in the electron density, and these have been applied to minerals (Perdew and Burke, 1996; Wang and Perdew, 1991; Wu and Cohen, 2006). However, although use of these advanced functionals leads to a general improvement in the quality of the

calculation, and in certain of the predicted structural and thermoelastic properties of minerals under high- P,T conditions, they do not always yield better predictions of specific observables including the vibrational dynamics, thermoelastic properties, or electronic properties (Payne et al., 1992).

2.09.3 Lattice Dynamics of Mantle Minerals

2.09.3.1 Diamond and (Mg,Fe)O Magnesio-wüstite

Diamond is only a minor mineral by abundance within the Earth; however, it is critically important to mantle research. Diamonds encapsulate mineral and fluid species formed at depth that are subsequently brought to the surface as inclusions during explosive eruptions. They thus provide a unique window into mantle mineralogy and geochemistry, with the deepest examples of mantle mineralogy brought to the surface (Harte and Harris, 1993, 1994; Kagi et al., 2000; Liu et al., 1990; Navon and Hutcheon, 1988; Sautter and Gillet, 1994; Sautter et al., 1991), and retain the memory of the conditions of entrapment (Gillet et al., 2002; Izreali et al., 1999; Sobolev et al., 2000). Some inclusions contain magnesio-wüstite ((Mg,Fe)O) and also (Mg,Fe)SiO₃ phases that may be derived *via* back transformation from silicate perovskite that are only stable below 670 km (Harris, 1992; Harte and Harris, 1993, 1994; McCammon, 2001). Inclusions of mantle minerals or C–O–H fluids are studied by microbeam FTIR or Raman spectroscopy: these provide valuable information on the nature of fluids at depth and the redox state of the mantle (Izraeli et al., 2001; Navon, 1991; Schrauder and Navon, 1993). Diamonds also provide unique high-strength and transparent anvil windows for DAC experiments, used to study mineral lattice dynamics and other properties in situ under mantle high- P,T conditions (Hemley and Mao, 2002; Hemley et al., 1987a).

Diamond possesses a cubic structure with space group $Fd\bar{3}m(O_h^7)$, with two atoms in its primitive cell (Figure 2). Diamond has the highest sound speeds of any material, has the highest bulk modulus value (K_0), has the highest thermal conductivity (κ) of all solids (Brüesch, 1982), and is the hardest known material (Brazhkin et al., 2002). The three optical phonons in Γ are triply degenerate, with symmetry label T_{2g} , giving a single peak in the Raman spectrum of diamond at 1332 cm⁻¹. This vibration involves a symmetric relative displacement of the C atoms in the unit cell about the inversion center. It does not result in any dipole moment change, and so the vibration is not IR-active. Overtone vibrations enabled by anharmonicity occur as broad features in both the Raman and the IR spectra of diamond in the 2200–2600 cm⁻¹ range (Gillet et al., 1998). These features can be used to deduce the form of $g(v)$ (Decius and Hexter, 1977). Other weak features observed in the IR spectra are typically due to various impurities, principally N and H (Clark et al., 1992).

The dispersion relations of diamond have been measured along various directions in reciprocal space using INS techniques on a large (254 ct) single crystal, at ambient P and T (Figure 2). The P and T dependence of the zone-center Raman-active phonon mode has been determined at up to $P=240$ GPa and $T=1900$ K (Bopp et al., 1985; Dubrovinskaia et al., 2010; Hanfland et al., 1985; Muinov et al., 1994; Zouboulis and Grimsditch, 1991). Gillet et al. (1998) analyzed the $(\partial v/\partial P)_T$ and $(\partial v/\partial T)_P$ data to obtain

the volume dependence of the diamond Raman mode frequency (Figure 3) and demonstrated its large intrinsic anharmonicity that likely extends to other vibrational modes of diamond.

(Mg,Fe)O magnesio-wüstite is the second most abundant phase in the Earth's lower mantle. Pure MgO (periclase) possesses the cubic B1 (NaCl) structure (space group $Fm\bar{3}m$) to at least 0.4 TPa (McWilliams et al., 2012), whereas FeO (wüstite) transforms first from B1 to a rhombohedral structure at $P>18$ GPa and then to the inverse NiAs structure (Mazin et al., 1998; Murakami et al., 2004b). The wüstite phase is usually slightly oxygen-deficient (i.e., FeO_{1-x}) at ambient pressure. Experiments indicate that Mg-rich (Mg,Fe)O is stable within the B1 structure throughout the P,T conditions of the lower mantle. Wüstite and iron-bearing solid solution undergo a spin transition in the pressure range 40–70 GPa at ambient temperature (Badro et al., 2003; Lin and Tsuchiya, 2008; Lin et al., 2003; Ohta et al., 2012; Tsuchiya et al., 2006).

As for diamond, there are two atoms in the primitive unit cell, so that the dispersion curves form both (TA and LA) acoustic and (TO and LO) optic branches (Figure 4). However, the bonding within these ionic crystals is now highly 'polar,' so that long-range Coulombic interactions also contribute substantially to the lattice dynamics. In the absence of any such electrostatic effects, the IR-active vibrational mode for MgO or FeO at the BZ center would be triply degenerate, that is, a single mode with F_{1u} symmetry. In fact, a single peak is observed in IR absorption studies, at ~ 380 cm⁻¹ (Gillet et al., 1998). However, the IR absorption technique only probes the TO lattice vibrations close to the BZ center. IR reflectance studies at ambient P indicate that a corresponding LO mode exists at a frequency of ~ 720 cm⁻¹ (Piriou and Cabannes, 1968). That observation results from the contribution of long-range Coulombic forces to the lattice dynamics that cause the LO mode to experience an additional restoring force. The phenomenon is termed 'TO-LO splitting,' and it occurs for all 'ionic' crystals, in response to the macroscopic electric field developed within polar solids (Ashcroft and Mermin, 1976; Born and Huang, 1954; Burns, 1985; Ferraro, 1984; Hofmeister, 1987, 1997; McMillan, 1985; McMillan and Hofmeister, 1988). The magnitude of the TO-LO splitting is correlated with the measured 'static' (i.e., ϵ_0 , in the limit that $\epsilon \rightarrow 0$ frequency, or $\Sigma(0)$) and high-frequency (Σ_∞) dielectric constants (with a limit in the high-frequency or optical range), *via* the Lyddane–Sachs–Teller (LST) relation:

$$\frac{\omega_{LO}}{\omega_{TO}} = \sqrt{\frac{\epsilon(0)}{\epsilon(\infty)}} \quad [17]$$

For complex minerals with n atoms in the primitive cell, the generalized LST relation becomes

$$\prod_{i=1}^{3n-3} \frac{\omega_{LO,i}}{\omega_{TO,i}} = \sqrt{\frac{\epsilon(0)}{\epsilon(\infty)}} \quad [18]$$

Here, the product runs over all optic modes (Gervais et al., 1973a,b; McMillan and Hofmeister, 1988). TO-LO splitting does occur not only for typically 'ionic' solids but also for any crystals that contain heteropolar bonding. For example, cubic moissanite (SiC) is isostructural with diamond and is usually

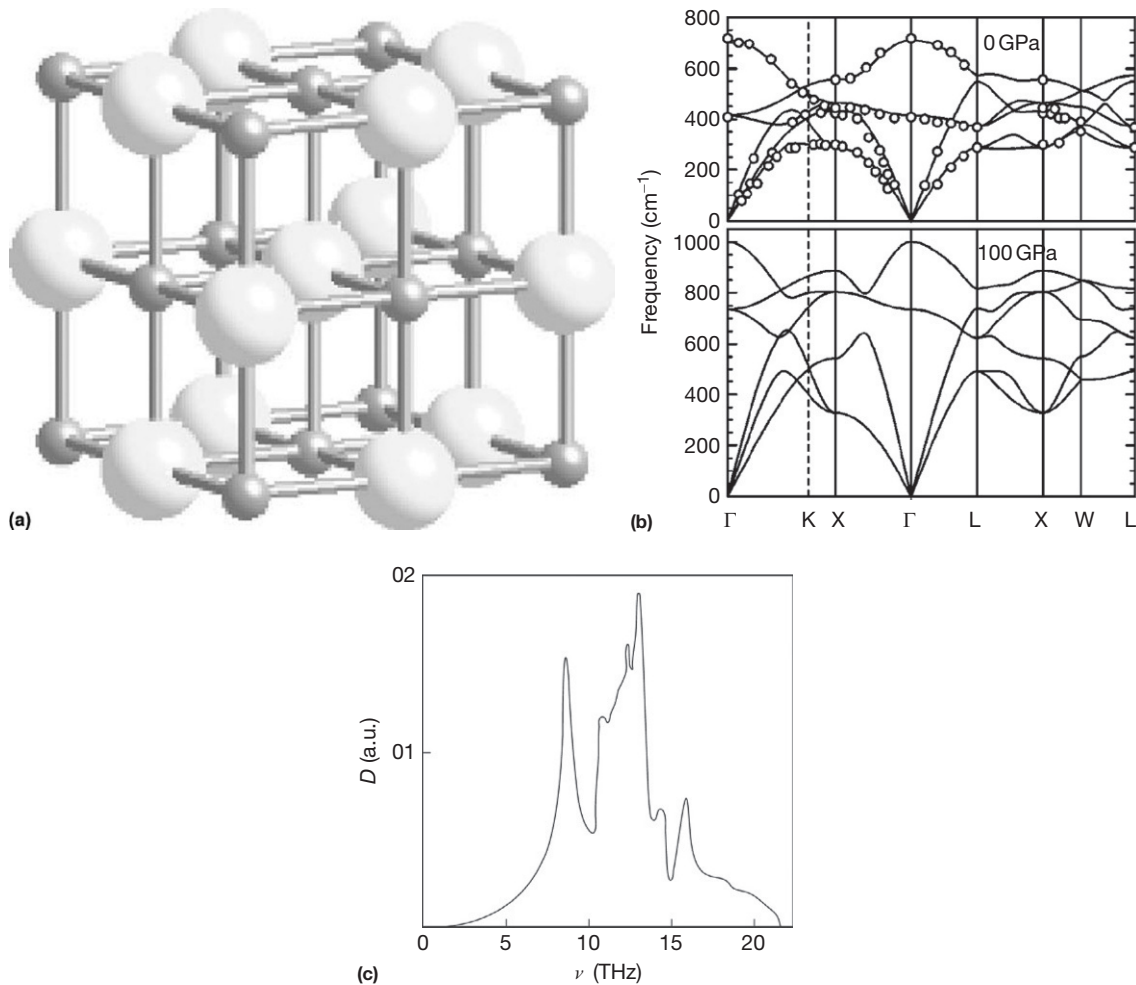


Figure 4 Structure and lattice dynamics in MgO. (a) The cubic B1-structured mineral MgO is dominated by ionic bonding interactions. (b) Dispersion relation of phonon at 0 and 100 GPa from DFT (Karki et al., 2000b) compared with ambient pressure INS data (Bilz and Kress, 1979). (c) The vibrational dispersion relations are averaged throughout the Brillouin zone to provide the vibrational density of states (VDOS) or $g(\nu)$ function. This constitutes the complete vibrational spectrum, which is deduced from INS experiments or obtained directly from ab initio calculations. Note that the vibrational frequencies in MgO are given here in THz units. (b) Reprinted from Karki BB, Wentzcovich RM, de Gironcoli S, and Baroni S (2000) High-pressure lattice dynamics and thermoelasticity of MgO. *Physical Review B* 61: 8793–8800. Copyrights (2000) by American Physical Society; (c) reprinted from Bilz H and Kress W (1979) *Phonon Dispersion Relations in Insulators. Springer Series on Solid-State Science*, Vol. 10, p. 50. Berlin: Springer. Copyright (1979) by Springer-Verlag (Berlin-Heidelberg).

considered to be covalently bonded. However, this phase exhibits a large TO–LO splitting of $\sim 180 \text{ cm}^{-1}$ (Bilz and Kress, 1979).

The phonon dispersion relations of MgO (Figure 4) and FeO are known from INS measurements (Bilz and Kress, 1979), as well as from various ab initio and first principles theoretical calculations that have been carried out to predict and model the thermoelastic properties under the high- P,T conditions of the deep mantle (Chizmeshya et al., 1994; Karki et al., 2000b; Oganov et al., 2005; Stixrude and Lithgow-Bertelloni, 2005; Stixrude et al., 1998).

The TO- and LO-mode anharmonic parameters of pure MgO have been measured experimentally to $T \sim 1000^\circ\text{C}$, using IR reflectance techniques at ambient P (Pirou and Cabannes, 1968). Ambient T and pressure shifts have been determined directly by IR transmission studies up to 22 GPa (Gillet et al., 1998; Figure 5). Information on the VDOS in MgO has also

been obtained at high P by examining the phonon sidebands on the Cr^{3+} luminescence in Cr^{3+} –MgO-doped crystals that were studied up to $P = 37 \text{ GPa}$ (Chopelas, 1992, 1996; Chopelas and Nicol, 1982). The TO-mode Grüneisen parameter obtained from the measurements was $\gamma \sim 1.5$ – 1.6 that lies close to the thermal value obtained from analysis of the thermodynamic properties ($\gamma_{\text{th}} = 1.52$) (Gillet et al., 1998). The TO- and LO-mode frequencies for FeO_{1-x} crystals occur at lower frequencies than for MgO, that is, at $\nu_{\text{TO}} \sim 300 \text{ cm}^{-1}$ and $\nu_{\text{LO}} \sim 530 \text{ cm}^{-1}$ at ambient P and T (Bilz and Kress, 1979).

2.09.3.2 (Mg,Fe)SiO₃ Perovskite, Postperovskite, and CaSiO₃ Perovskite

MgSiO₃ perovskite is formed by transformations of lower-pressure magnesium silicates above $P = 22$ – 24 GPa ; its appearance along with that of (Mg,Fe)O magnesiowüstite is thought to mark the 660–670 km seismic discontinuity that defines the

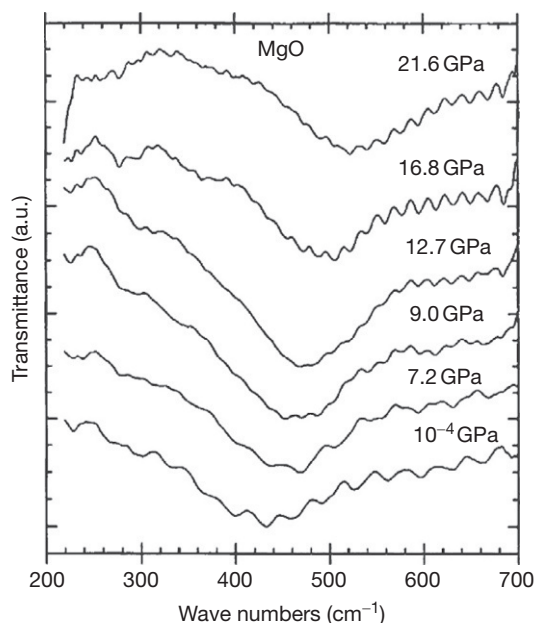


Figure 5 High-pressure IR transmission spectra of MgO to $P \approx 22$ GPa (Gillet et al., 1998). Here, the vibrational energy scale is shown in cm^{-1} ($1 \text{ cm}^{-1} = 2.998 \text{ THz}$, for comparison with the data in Figure 6). The main band is broad and corresponds to the IR absorption associated with the TO mode. The weak 'fringes' in the data set are due to IR interference effects, associated with the thickness of the sample. The initial data were obtained by Grzechnik et al. (1999), and the diagram shown here is reprinted from Gillet P, Hemley RJ, and McMillan PF (1998) *Vibrational properties at high pressures and temperatures*. In: Hemley RJ (ed.) *Ultrahigh-Pressure Mineralogy. Reviews in Mineralogy*, Vol. 37, p. 575. Washington, DC: Mineralogical Society of America, with permission. Copyright (1998) by the Mineralogical Society of America.

onset of the lower mantle (Anderson, 1989; Bina, 1998; Jeanloz and Thompson, 1983; Knittle and Jeanloz, 1987; Liu, 1974, 1975; Liu and Bassett, 1986; Ringwood, 1962, 1975). It then likely remains stable throughout nearly the entire P,T range of the lower mantle, to result in the predominant mineral phase within the Earth (Ringwood, 1962). MgSiO_3 perovskite has not yet been observed in any natural samples, although $(\text{Mg,Fe})\text{SiO}_3$ phases that might constitute its decompression products have been identified in deep diamond inclusions (Harte and Harris, 1994) and meteorites (Sharp et al., 1997; Tomioka and Fujino, 1997). The silicate perovskite phase has been synthesized and recovered to ambient conditions in various studies designed to establish its vibrational, elastic, and thermodynamic properties (Durben and Wolf, 1992; Hemley and Cohen, 1992; Hemley et al., 1989; Williams et al., 1987). The lattice dynamics and thermophysical behavior of MgSiO_3 perovskite have been studied extensively using first principles methods to determine the phonons and thermoelastic properties under a wide range of mantle P,T conditions (Karki et al., 2000a, 2001; Oganov et al., 2000; Wentzcovich et al., 2004a).

The type mineral phase that gives rise to the name perovskite is CaTiO_3 , originally thought to possess a cubic structure ($Fm\bar{3}m$), the ideal perovskite aristotype. In fact, CaTiO_3 is determined to possess an orthorhombic structure with space group $Pbnm$, which is also the structure of MgSiO_3 perovskite at

ambient and high- P,T conditions relevant to the lower mantle (Hemley and Cohen, 1992; Serghiou et al., 1998; Shim et al., 2001). Perovskite-structured solids have a general composition ABX_3 ; they are constructed from corner-linked BX_6 octahedral units, with the A cations occupying 12-coordinated sites within the ideal cubic structure. The A-site coordination becomes lowered for distorted perovskite structures; for example, the Mg^{2+} cations in MgSiO_3 perovskite are eightfold coordinated. Perovskite-structured materials exhibit a wide range of structure types and symmetries derived from distortions of the cubic aristotype. The largest family of these occurs due to concerted rotations of the linked BX_6 octahedra about their highly flexible B–X–B linkage (i.e., the interoctahedral Mg–O–Mg linkage, in the case of MgSiO_3 perovskite; Figure 6). Various coupled rotations in + or – directions result in a large variety of tetragonal, orthorhombic, and trigonal structures (Darlington, 2002; Glazer, 1972, 1975). Other structural distortions involve displacements of the A or B cations away from their central positions within the octahedral or larger polyhedral sites. These structural distortions are driven by soft phonon modes that mainly occur at the BZ boundaries (Figure 6), for example, at the R or M points of the cubic perovskite unit cell (Hemley and Cohen, 1992; Wolf and Bukowinski, 1987; Wolf and Jeanloz, 1985).

Theoretical calculations and experimental x-ray determinations of MgSiO_3 perovskite under deep mantle high- P,T conditions now indicate that phase transitions associated with lattice dynamics instabilities are unlikely to be present throughout the P,T range of the lower mantle (Karki et al., 2000a; Oganov et al., 2000, 2005; Shim et al., 2001). Displacive transformations within orthorhombic MgSiO_3 perovskite would occur at such high- P,T conditions that they would be first intersected by first-order phase transitions, including melting (Akins et al., 2004; Hemley and Kubicki, 1991; Zerr and Boehler, 1993), or transformation into the CaIrO_3 -structured postperovskite phase at high pressure (Murakami et al., 2004a; Oganov and Ono, 2004; Tsuchiya et al., 2004c, 2005).

Raman and IR spectra at ambient P and T have been determined experimentally for pure MgSiO_3 perovskite for various samples recovered from high- P,T synthesis experiments (Hemley and Cohen, 1992; Hemley et al., 1989; Lu et al., 1994; Weng et al., 1983; Williams et al., 1987; Wolf and Jeanloz, 1985; Figure 7). Recent first principles calculations reproduce the experimentally determined frequencies to within a few percent, which is typical for such experiment-theory comparisons (Karki et al., 2001; Wentzcovich et al., 2004a). Both the theoretical results and the experimental measurements are subject to uncertainty, and the experiments are generally carried out at $T = 300 \text{ K}$, whereas the calculations are static. All of the Raman and IR modes at the BZ center at ambient P,T conditions have now been definitely identified (Caracas and Cohen, 2006; Karki et al., 2000a; Wentzcovich et al., 2004). Raman and IR spectra of the MgSiO_3 perovskite phase have been measured experimentally to $P = 65 \text{ GPa}$ at ambient T , at high T (metastably) at ambient $P,T = 600 \text{ K}$, and now under simultaneous high- P,T conditions (Chopelas, 1996; Durben and Wolf, 1992; Gillet et al., 2000b; Hemley et al., 1989; Liu et al., 1994; Wang et al., 1994; Williams et al., 1987) and reproduced accurately by first principles simulations (Caracas and Cohen, 2006).

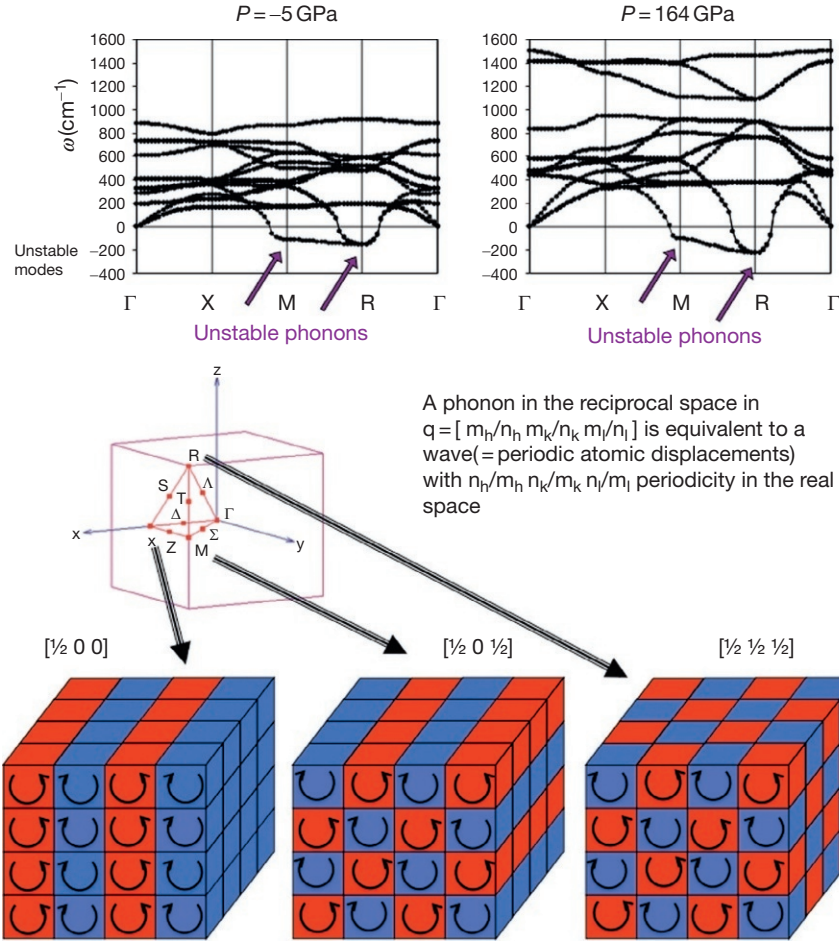


Figure 6 Structure and lattice dynamics of the cubic perovskite aristotype ($Pm\bar{3}m$ symmetry) of CaSiO_3 perovskite (modified from Caracas R (2005) *CaSiO}_3* perovskite at lower mantle pressures. *Geophysical Research Letters* 32: L06306). The interoctahedral linkages are flexible, and imaginary frequency vibrations are associated with coupled rotational modes around various crystallographic axes that result in soft-mode behavior and structural distortions away from cubic symmetry shown as rotation patterns and domains with opposite directions (blue and red). The octahedral rotation modes propagate along various different directions in reciprocal space, to yield different symmetry points at the Brillouin zone boundary. Lattice dynamics calculated for the cubic perovskite structure of CaSiO_3 showed several unstable phonon branches along various directions in reciprocal space, especially along the Γ -M ($\xi, \xi, 0$) and Γ -R (ξ, ξ, ξ) directions, resulting in lattice distortions with tetrahedral symmetry. In MgSiO_3 , perovskite adopts the orthorhombic ($Pbnm$) symmetry due to further distortions.

The cubic perovskite aristotype with space group $Fm\bar{3}m$ has no Raman-active modes; only three triply degenerate IR-active vibrations exist at the BZ center. Symmetry analysis yields

$$\Gamma_{\text{vib}} = 3F_{1u}(\text{IR}) + F_{2u}(\text{inactive}) \quad [19]$$

The reduction of the perovskite symmetry to the orthorhombic space group $Pbnm$ with $Z=4$ MgSiO_3 units in the primitive cell causes a splitting of the IR-active modes, the occurrence of additional peaks in the IR spectrum, and the appearance of a first-order Raman spectrum (Figure 7):

$$\begin{aligned} \Gamma_{\text{vib}} = & 7A_g(R) + 7B_{1g}(R) + 5B_{2g}(R) + 5B_{3g}(R) \\ & + 8A_u(\text{inactive}) + 7B_{1u}(\text{IR}) + 9B_{2u}(\text{IR}) + 9B_{3u}(\text{IR}) \end{aligned} \quad [20]$$

The first observations of a Raman spectrum for MgSiO_3 perovskite immediately confirmed its reduction in symmetry to an orthorhombic structure (space group $Pbnm$) suggested by x-ray diffraction (Hemley et al., 1989; Williams et al., 1987).

Apparent discrepancies between theory and experiment, including missing IR and Raman modes (McMillan et al., 1996b), have now been resolved by accurate first principles calculations (Caracas and Cohen, 2006).

The phonon dispersion relations or $g(v)$ functions for MgSiO_3 perovskite have not yet been measured experimentally; however, the lattice dynamics have been calculated theoretically by first principles methods over a wide P, T range (Figure 8), and the results have been used to predict thermophysical properties relevant to the lower mantle (Hemley and Cohen, 1992; Karki et al., 2000a; Oganov et al., 2000; Wentzcovich et al., 2004a). These calculations are known to be accurate up to arbitrarily high P ; however, they do not fully take into account the thermodynamic properties at high T , because intrinsic phonon anharmonicity is ignored within the QH approximation. Gillet et al. (2000b) analyzed the Raman spectra obtained at high P and low T to evaluate the intrinsic anharmonicity contributions to the

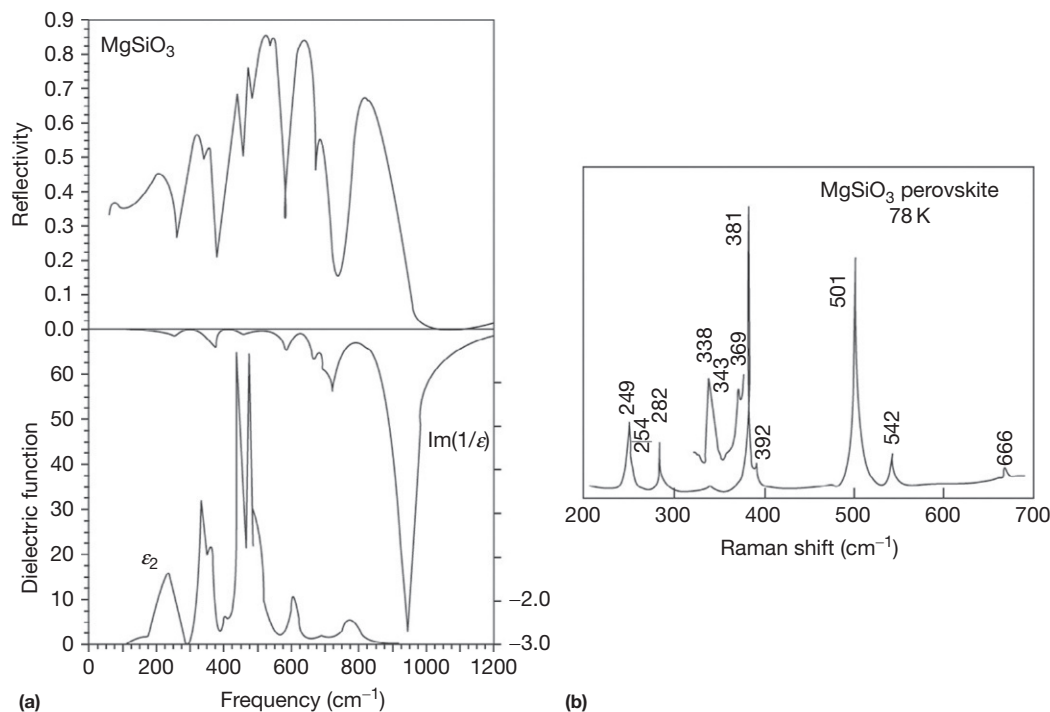


Figure 7 Infrared and Raman spectra of MgSiO₃ perovskite recorded at ambient pressure. (a) Infrared reflectivity data (modified from Lu R, Hofmeister AM, and Wang YB (1994) Thermodynamic properties of ferromagnesium silicate perovskites from vibrational spectroscopy. *Journal of Geophysical Research B* 99: 11795–11804). Peaks and minima in the dielectric functions $\epsilon_2(\nu)$ and $\text{Im}(1/\epsilon(\nu))$ indicate the positions of TO- and LO-mode frequencies, respectively. (b) The Raman spectrum was obtained for a sample cooled to 78 K (Durben and Wolf, 1992). The existence of a first-order Raman spectrum indicates the presence of an orthorhombic distortion of the perovskite structure (reprinted from Durben DJ and Wolf GH (1992) High-temperature behavior of metastable MgSiO₃ perovskite: A Raman spectroscopic study. *American Mineralogist* 77: 890–893, with permission. Copyright (1992) by the Mineralogical Society of America).

lattice dynamics and thermophysical properties of MgSiO₃ perovskite. Also, Lu et al. (1994) obtained data on the intrinsic anharmonicity of IR-active modes, from the analysis of the IR reflectivity spectrum. The spectroscopy data and first principles calculations were used to construct $g(\nu)$ functions in order to calculate the heat capacity (C_v and C_p) and the vibrational entropy (S) as a function of T ; the thermodynamic data were used to demonstrate the general nature of negative P,T Clapeyron slopes involving perovskite-forming reactions in the mantle (Akaogi and Ito, 1993; Lu et al., 1994; Navrotsky, 1980, 1989).

Most experimental and theoretical studies of the lattice dynamics of MgSiO₃ perovskite have focused on the end-member phase. However, the mineral present within the lower mantle is likely to exist as a solid solution within the (Mg,Fe,Al)(Al,Si)O₃ system that might contain vacancies and chemical substitutions on cation and anion sites. These substitutions could have large effects on the thermophysical properties of silicate perovskites, as well as their phase transitions (Caracas, 2005; Wood and Rubie, 1996). Lu et al. (1994) and Wang et al. (1994) determined IR and Raman spectra for (Mg,Fe)SiO₃ perovskites recovered from high- P,T experiments; they found only small changes in the spectra upon Fe²⁺/Mg²⁺ substitution, but the Raman peaks were substantially broadened, due to Mg/Fe structural disorder on the cation sites. The frequencies were all slightly shifted to lower wave number in consistency with the small lattice expansion that occurs within

the Fe/Mg perovskite series (Kudoh et al., 1990; Mao et al., 1991; Wang et al., 1994).

At conditions of the base of the Earth's mantle, MgSiO₃ transforms into a new postperovskite phase with the CaIrO₃ structure that contains edge-shared SiO₆ units arranged into layers (Murakami et al., 2004a; Oganov and Ono, 2004; Tsuchiya et al., 2004c). The formation of this layered structure is expected to have a large effect on the elastic anisotropy and the thermophysical properties developed at the base of the lower mantle and within the D' layer (Hernlund et al., 2005; Wookey et al., 2005). The postperovskite transition is now also observed to occur for perovskite-structured materials with (Mg,Fe)SiO₃ compositions. Al³⁺ incorporation into the silicate perovskite phase is also found to affect the P and T regime for the transition (Caracas and Cohen, 2007a). The vibrational spectrum of MgSiO₃ in its CaIrO₃-structured phase has not yet been measured experimentally, but it has been computed by several groups using a variety of functionals and DDFT packages (Caracas and Cohen, 2006; Figure 9). Its lattice dynamics and thermoelastic properties have been predicted theoretically using first principles methods, under high- P conditions extending to those at the base of the mantle (Tsuchiya, 2005; Wentzcovitch et al., 2006). Raman spectra have been obtained on the germanate analog MgGeO₃ to over 120 GPa (Shim et al., 2007).

A CaSiO₃ perovskite phase is also expected to be present within the lower mantle (Hemley and Cohen, 1992; Liu and

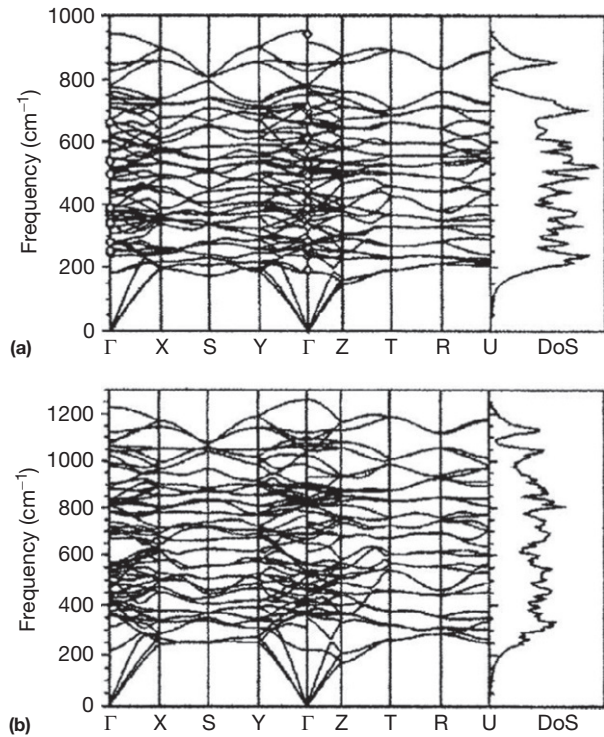


Figure 8 Lattice dynamics calculated using accurate first principles methods for MgSiO_3 perovskite (a) at ambient pressure and (b) at $P = 100$ GPa (Karki et al., 2000a). Experimentally observed frequency values taken from IR and Raman data at ambient P are shown as circles on the axis at the Γ point. Reprinted from Karki BB, Wentzcovich RM, de Gironcoli S, and Baroni S (2000) *Ab initio* lattice dynamics of MgSiO_3 -perovskite at high pressure. *Physical Review B* 62: 14750–14756, with permission. Copyright (2000) by the American Physical Society.

Ringwood, 1975). This material was originally expected to remain cubic throughout all relevant mantle P, T conditions. However, it is now recognized that a slight tetragonal distortion should occur at pressures below $P \sim 14$ GPa, driven by phonon-mode instabilities (Caracas, 2005; Chizmeshya et al., 1996; Hemley and Cohen, 1992; Jung and Oganov, 2005; Stixrude et al., 1996), while all the other symmetry allowed distortions having higher energies. The tetragonal structure results as a condensation of the unstable phonon mode in the $\mathbf{q} = \mathbf{R}$ point of the cubic Brillouin zone, namely, the corner of the reciprocal cube. This mode corresponds to in-phase rigid rotations of the octahedra parallel to the Cartesian axis (Figure 6). The CaSiO_3 phase cannot normally be recovered to ambient P, T conditions for study; instead, it amorphizes during decompression. This phenomenon is attributed to the collective freezing-in of the unstable phonon branches in CaSiO_3 perovskite parallel to the edges of the Brillouin zone (Caracas, 2005; Stixrude et al., 1996).

2.09.3.3 Stishovite and Poststishovite SiO_2 Polymorphs

The α -quartz phase of SiO_2 is abundant at the Earth's surface, and its lattice dynamics have been thoroughly studied by theory and experimental studies, including IR, Raman, and INS techniques, and measurements carried out at high T and high P (Dolino and Bachheimer, 1977; Dolino et al., 1983; Gervais

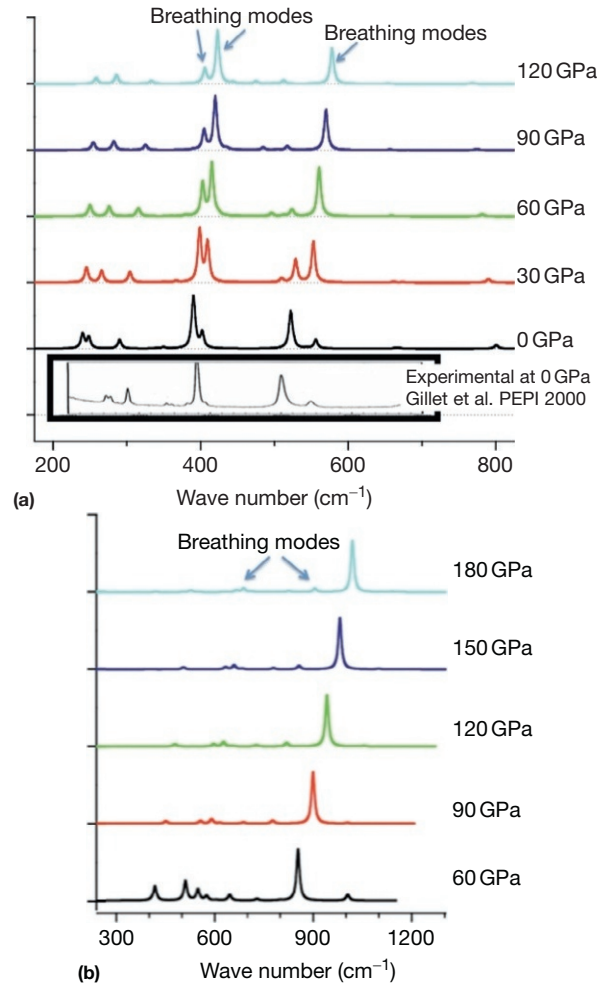


Figure 9 Calculated powder Raman spectra of the (a) perovskite and (b) postperovskite (CaIrO_3) structure of MgSiO_3 at mantle pressures (modified from Caracas R and Cohen RE (2006) Theoretical determination of the Raman spectra of MgSiO_3 perovskite and post-perovskite at high pressure. *Geophysical Research Letters* 33. doi: 10.1029/2006gl025736). The low-pressure spectrum of MgSiO_3 perovskite (Gillet et al., 2000b) is shown for comparison.

and Piriou, 1975; Ghose, 1985, 1988; Shapiro et al., 1967). The principles of soft-mode lattice dynamics behavior were first defined in quartz, where the low-lying Raman-active mode at 206 cm^{-1} at ambient P and T shifts rapidly and asymptotically to approach zero frequency at $T = 858 \text{ K}$, at the temperature of the displacive α - β quartz transition. That process was first noted and described by Raman and Nedungadi (1940) and has become a classic example of a second-order displacive phase transformation driven by a vibrational soft mode (Decius and Hexter, 1977; Ghose, 1985; McMillan, 1985, 1989; Raman and Nedungadi, 1940; Scott, 1974). The interactions between lattice dynamics and structural and elastic properties for quartz at high T are now known to be considerably more complex than this simple picture allows, however (Dolino and Bachheimer, 1977; Dolino et al., 1983).

At above $P \sim 9$ GPa, SiO_2 transforms into the mineral phase stishovite (rutile structure) that contains octahedrally

coordinated Si^{4+} ions (Stishov and Popova, 1961). Stishovite could be present as a free SiO_2 phase throughout the mantle, especially in basaltic compositions (Funamori et al., 2000; Kesson et al., 1994; Kingma et al., 1995). The natural occurrence of stishovite was first described as a product of impact metamorphism (Chao et al., 1962); it has now also been recorded within highly metamorphosed deep crustal rocks (Liou et al., 1998).

The zone-center vibrational modes for rutile-structured SiO_2 stishovite are

$$\Gamma_{\text{vib}} = A_{1g}(R) + A_{2g}(\text{inactive}) + B_{1g}(R) + B_{2g}(R) + E_g(R) + 2B_{1u}(\text{IR}) + 3E_u(\text{IR}) \quad [21]$$

Raman spectra (Hemley et al., 1986) for both natural and synthetic stishovite samples showed all four expected modes, and their pressure derivatives have been studied experimentally and theoretically (Hemley, 1987; Figure 10). Early IR transmission data (Lyon, 1962) were distorted due to optical effects within the highly refractive mineral, as shown by subsequent reflectivity studies (Hofmeister, 1996; Hofmeister et al., 1990; McMillan and Hofmeister, 1988; Figure 10). Pressure shifts of the IR-active modes were recorded by Hofmeister (1996) and Williams et al. (1993), and the T dependence of the Raman spectrum was investigated by Gillet et al. (1990, 1998).

The Raman spectrum of stishovite at ambient P and T contains one low-frequency mode with B_{1g} symmetry (231 cm^{-1}) that shifts to lower wave number with increasing P (Hemley, 1987; Kingma et al., 1995). The atomic displacements associated with that mode correspond to those required to transform the structure into a CaCl_2 -structured polymorph, *via* a second-order displacive phase transition (Cohen, 1992; Hemley, 1987; Kingma et al., 1995; Nagel and O'Keeffe, 1971; Peercy and Morosin, 1973; Samara and Peercy, 1973). A phonon-driven rutile- CaCl_2 phase transition for SiO_2 has been predicted by theoretical calculations (Cohen, 1991, 1992; Lacks and Gordon, 1993; Lee and Gonze, 1995; Matsui and Tsuneyuki, 1992), and it was observed to occur experimentally at $P \sim 50$ GPa, using a combination of in situ Raman spectroscopy and x-ray diffraction techniques (Andrault et al., 1998; Kingma et al., 1995; Murakami et al., 2003; Shieh et al., 2005; Figure 10).

A SiO_2 polymorph with orthorhombic $\alpha\text{-PbO}_2$ structure has also been identified in various run products from high- P,T experiments and in natural meteorite samples: the phase appears to become stable above $P \sim 90$ GPa (Dera et al., 2002; Dubrovinskaia et al., 2001; Dubrovinsky et al., 1997, 2003; El Goresy et al., 1998; Murakami et al., 2003; Sharp et al., 1999; Shieh et al., 2005; Tsuchida and Yagi, 1989, 1990; Tsuchiya et al., 2004b). Another monoclinic SiO_2 phase with the baddeleyite (ZrO_2) structure has also been identified in meteorites (El Goresy et al., 2000). Micro-Raman spectroscopy is usefully combined with x-ray diffraction and transmission electron microscopy to experimentally characterize such new high-pressure polymorphs of SiO_2 . The likely stability ranges of CaCl_2 - and $\alpha\text{-PbO}_2$ structured SiO_2 under deep mantle conditions have been investigated and discussed (Shieh et al., 2005). Other high-density forms of SiO_2 have been predicted by theoretical calculations, formed *via* lattice dynamics instabilities occurring at low T within low-pressure structures

(Badro et al., 1997; Teter et al., 1998; Tsuchiya et al., 2004a; Wentzcovich et al., 1998). However, it is unlikely that these metastable phases would be achieved or, if formed, that they could persist over geologic timescales under the high- P,T conditions attained within the mantle (Shieh et al., 2005).

2.09.3.4 $(\text{Mg,Fe})_2\text{SiO}_4$ Olivine, Wadsleyite, and Ringwoodite

Olivine with composition near $(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$ dominates the mineralogy of the upper mantle. The vibrational modes of end-member Mg_2SiO_4 (forsterite) and Fe_2SiO_4 (fayalite) have been studied extensively using IR and Raman spectroscopies. Vibrational dynamics in forsterite and fayalite samples have also been investigated by INS techniques, and theoretical calculations of the lattice dynamics have been carried out (Choudhury et al., 2002; Durben et al., 1993; Hofmeister, 1987, 1997; Hofmeister et al., 1989; Iishi, 1978; McKeown et al., 2010; McMillan, 1985; McMillan and Hofmeister, 1988; McMillan et al., 1996b; Piriou and McMillan, 1983; Price et al., 1987, 1991; Rao et al., 1988; Servoin and Piriou, 1973). Studies have been carried out in situ at high- P conditions, at high- T conditions, and under simultaneous high- P,T conditions; the results were used to predict and interpret the high- P,T thermoelastic properties and vibrational mode anharmonicity (Chopelas, 1990; Gillet et al., 1991, 1997, 1998; Hofmeister, 1987, 1997; Hofmeister et al., 1989; Reynard et al., 1992; Wang et al., 1993).

The full set of IR- and Raman-active modes for Mg_2SiO_4 forsterite and Fe_2SiO_4 fayalite have been assigned experimentally *via* single-crystal measurements (Hofmeister, 1987; Iishi, 1978; McMillan, 1985; McMillan and Hofmeister, 1988; Piriou and McMillan, 1983; Servoin and Piriou, 1973). The $g(v)$ functions are determined from INS measurements (Chaplot et al., 2002; Choudhury et al., 2002; Price et al., 1991; Rao et al., 1988). Both experimentally modeled and theoretically predicted VDOS functions have been used to carry out calculations of the high- P,T specific heat and entropy, leading to various predictions and a new understanding of phase transformations among the Mg_2SiO_4 polymorphs, and also the thermal conductivity of mantle phases, throughout the conditions of the upper mantle (Akaogi et al., 1984; Choudhury et al., 1998, 2002; Gillet et al., 1997, 1998; Hofmeister, 1999; Hofmeister et al., 1989; Rao et al., 1988).

Above $P \sim 13\text{--}15$ GPa, $(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$ olivine transforms into spinel-structured polymorphs (Agee, 1998; Akaogi et al., 1989; Bina and Wood, 1987; Gasparik, 1990; Rigden et al., 1991). These transitions mark the onset of the mantle 'transition zone' at ~ 410 km depth, associated with an abrupt increase in the seismic velocities. Pure Fe_2SiO_4 olivine transforms directly to a spinel structure at $P \sim 6\text{--}7$ GPa. However, Mg_2SiO_4 does not transform directly into the spinel-structured $\gamma\text{-Mg}_2\text{SiO}_4$ phase (ringwoodite), but it first exhibits a transformation to a $\beta\text{-Mg}_2\text{SiO}_4$ (wadsleyite) phase (Akaogi et al., 1984, 1989; Bina and Wood, 1987; Katsura and Ito, 1989; Wu et al., 1993). In an early application of Kieffer's model to mantle mineralogy, Akaogi et al. (1984) obtained IR and Raman data for the α - (olivine), β -, and γ -polymorphs of Mg_2SiO_4 and constructed a model $g(v)$ function to calculate the heat capacity and entropy. The results were combined with calorimetric data to predict P,T boundaries between Mg_2SiO_4 phases

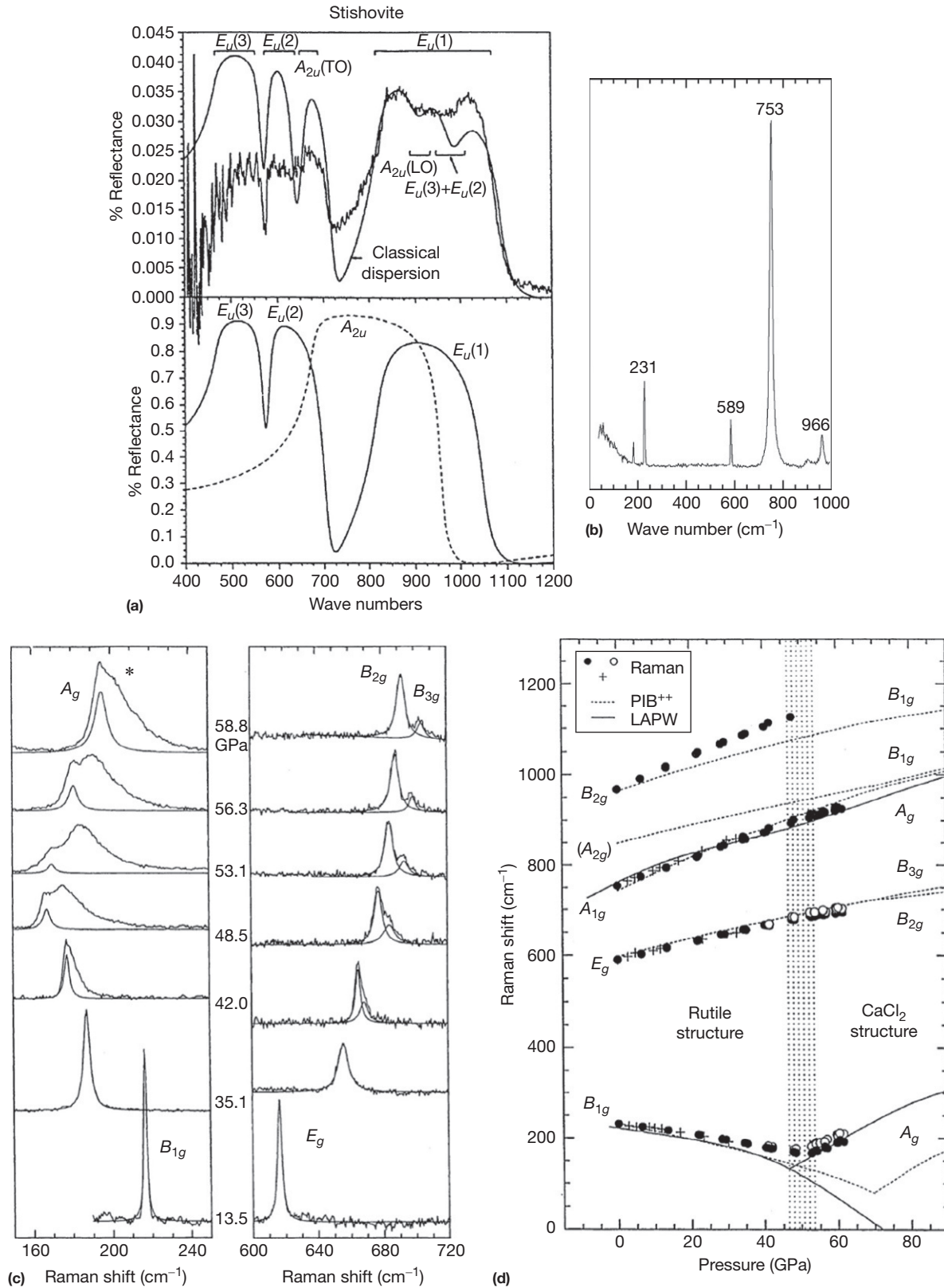


Figure 10 Infrared and Raman spectra of SiO_2 stishovite and Raman data for the CaCl_2 -structured phase (Hemley, 1987; Hemley et al., 1986; Hofmeister, 1996; Hofmeister et al., 1990; Kingma et al., 1995). (a) The unpolarized IR reflectance spectrum of a polycrystalline sample of SiO_2 stishovite is shown at top, along with the TO- and LO-mode frequencies obtained from the analysis of the reflectivity data. The synthetic spectrum at the bottom was then reconstructed using these parameters, for both predicted mode symmetries (A_{2u} and E_u) (Hofmeister et al., 1990). (b) Raman

(Akaogi et al., 1984). The first results have now been updated (Akaogi et al., 1989; Chopelas, 1990, 1991; Gillet et al., 1997; Hofmeister et al., 1989).

Powder IR spectrum for Fe_2SiO_4 spinel or ahrensite (Ma et al., 2013) showed three peaks occurring at 848, 503, and 344 cm^{-1} (Jeanloz, 1980). IR reflectance data were recorded over a similar frequency range (McMillan and Hofmeister, 1988; McMillan et al., 1996b). IR reflectance spectrum of analog Ni_2SiO_4 spinel showed the four bands expected from group theory (Reynard, 1993). The broad highest-frequency band is due to the ν_3 asymmetric stretching vibration of tetrahedral SiO_4 units with a large TO–LO splitting. The midrange mode corresponds to the IR-active SiO_4 deformation (ν_4), with mainly octahedral $\text{MgO}_6/\text{FeO}_6$ stretching vibrations in the lower frequency range; some coupling is expected to occur among these various vibrational modes (Akaogi et al., 1984; Jeanloz, 1980; McMillan and Hofmeister, 1988; McMillan et al., 1996b). ν_4 occurs at 503 cm^{-1} for $\gamma\text{-Fe}_2\text{SiO}_4$ and at 445 cm^{-1} for $\gamma\text{-Mg}_2\text{SiO}_4$. A further peak is observed at 240 cm^{-1} in the IR transmission spectrum for $\gamma\text{-M}_2\text{SiO}_4$ (Akaogi et al., 1984).

Raman spectra for Mg_2SiO_4 spinel (Akaogi et al., 1984; McMillan and Akaogi, 1987) show strong peaks at 794 and 836 cm^{-1} , determined to correspond to the symmetric (ν_1) and asymmetric (ν_3) stretching vibrations of the SiO_4 tetrahedra (Chopelas et al., 1994). Additional weak peaks at 600, 370, and 302 cm^{-1} were assigned to Raman-active modes associated with the ν_2 and ν_4 SiO_4^{4-} deformation modes and MgO_6 vibrations (Chopelas et al., 1994; McMillan and Akaogi, 1987). The pressure shifts were measured in the study to 20 GPa (Chopelas et al., 1994). The lattice dynamics of $\gamma\text{-Mg}_2\text{SiO}_4$ have been studied theoretically using empirical potential methods (Matsui and Busing, 1984; Price et al., 1987).

The $\beta\text{-(Mg,Fe)}_2\text{SiO}_4$ polymorph (i.e., ‘wadsleyite’; also referred to as ‘modified spinel,’ or ‘ β -phase,’ in earlier studies) is expected to be a dominant mineral between 410 and 520 km depth. Akaogi et al. (1984) obtained the first IR spectrum of $\beta\text{-Mg}_2\text{SiO}_4$. The IR and Raman spectra of $\beta\text{-Mg}_2\text{SiO}_4$ are now characterized both at ambient P, T and under high- T and high- P conditions, and their lattice dynamics have been investigated using empirical potentials (Chopelas, 1991; Cynn and Hofmeister, 1994; McMillan and Akaogi, 1987; Price et al., 1987; Reynard and Rubie, 1996). At variance of the olivine- and spinel-structured orthosilicates, the IR and Raman spectra of wadsleyite show peaks in the $600\text{--}800\text{ cm}^{-1}$ range diagnostic of the Si–O–Si linkages of the Si_2O_7 units (Chopelas, 1991; Cynn and Hofmeister, 1994; McMillan and Akaogi, 1987; McMillan et al., 1996b; Reynard et al., 1996). The resulting crystallographic sites could provide important hosts for OH

species in the mantle (Cynn and Hofmeister, 1994; Kohlstedt et al., 1996; McMillan and Hofmeister, 1988; Smyth, 1987).

First principles calculations of the phonon dispersion relations were calculated using DFPT techniques for the three polymorphs of Mg_2SiO_4 . They allowed the computation of the phonon band dispersion relations and from there of the total VDOS. The two formalisms for the exchange–correlation, LDA and GGA, employed for building the theoretical phase diagram allow bracketing the experimental phase boundaries (Yu et al., 2008).

2.09.3.5 Pyroxenes

Compared with $(\text{Mg,Fe})_2\text{SiO}_4$ structures, there have been fewer vibrational data obtained, or theoretical lattice dynamics calculations carried out, for the complex pyroxene solid solutions that provide the most important group of upper mantle minerals next to olivine. Raman studies of these solid solutions were performed for the purpose of phase identification (Huang et al., 2000; Ma et al., 2009; Noguchi et al., 2012; Tribaudino et al., 2012). Ca-rich clinopyroxenes have not attracted much attention because diopside remains in the $C2/c$ space group in the upper mantle. The Raman and IR spectra of the monoclinic pyroxene diopside ($\text{CaMgSi}_2\text{O}_6$), present within the upper mantle, are well known from single-crystal measurements, combined with empirical force field calculations (Dowty, 1987; Etchepare, 1970; Zulumyan et al., 1976); Raman spectra for this phase have been measured to $P=16\text{ GPa}$ (Chopelas and Boehler, 1992).

MgSiO_3 (enstatite) exhibits complex polymorphism among various crystal structures as a function of P and T (Angel et al., 1992; Angel and Hugh-Jones, 1994; Choudhury et al., 2002; Gasparik, 1990; Kanzaki, 1991a; McMillan et al., 1996b; Pacalo and Gasparik, 1990; Prewitt and Downs, 1998; Yang and Ghose, 1994; Yang and Ghose, 1995). The assignment of the various phase boundaries and the recognition of stable versus metastable phases in enstatite have been quite controversial. Studies of the lattice dynamics using INS methods combined with MD simulations have now advanced our understanding of the system (Chaplot and Choudhury, 2001; Chaplot et al., 2002; Choudhury and Chaplot, 2000; Choudhury et al., 2002). It now appears likely that the stable phase at ambient P and T is orthoenstatite (space group $Pbca$). Polarized Raman spectra and INS data for this phase have been obtained (Choudhury et al., 1998).

At high temperature ($T>800\text{ K}$), a first-order transformation into the protoenstatite phase ($Pbcn$ symmetry) occurs at ambient P (Choudhury and Chaplot, 2000). Brillouin spectroscopic investigation of elastic behavior during this first-order phase transition suggested the existence of a hidden second-order

spectrum of synthetic stishovite showing the four expected peaks at 231, 589, 753, and 966 cm^{-1} . The presented spectrum can be obtained at <http://www.ens-lyon.fr/LST/Raman/>. The Raman spectra of stishovite were first obtained on natural and synthetic samples (Hemley et al., 1986). (c) Raman spectra obtained in situ at high pressure by Kingma et al. (1995) showed evidence for softening of the lowest-frequency B_{1g} mode, resulting in a transition to CaCl_2 -structured SiO_2 at $P\sim 50\text{ GPa}$ pressure. (d) The mode softening in SiO_2 stishovite and its transformation to the CaCl_2 structure were predicted by first principles theoretical calculations and was confirmed by experimental measurements (Cohen, 1992; Kingma et al., 1995). The original data for this figure were presented by Kingma et al. (1995). (a) Reprinted from Hofmeister A, Xu J, and Akimoto S (1990) Infrared spectroscopy of synthetic and natural stishovite. *American Mineralogist* 75: 951–955, with permission. Copyright (1990) by the Mineralogical Society of America. (c and d) Reprinted from Gillet P, Hemley RJ, and McMillan PF (1998) Vibrational properties at high pressures and temperatures. In: *Ultra-high Pressure Mineralogy: Physics and Chemistry of the Earth's Deep Interior. Reviews in Mineralogy*, Vol. 37, p. 555, with permission. Copyright (1998) by the Mineralogical Society of America.

transition to a guessed *Cmca* symmetry polymorph masked by the first-order transition to protoenstatite (Jackson et al., 2004). This complex transitional scheme was also observed by Raman and Brillouin spectroscopies on natural iron-bearing enstatite, used to decipher the high-temperature ($T > 1400$ K) phase diagram of enstatite where the protoenstatite phase is stable only up to 1 GPa, and replaced by the polymorph of possible *Cmca* symmetry at higher pressures (Reynard et al., 2010). The second-order phase transition produces a marked elastic softening, as well as a softening of low-frequency Raman modes (Jackson et al., 2004; Reynard et al., 2010; Sharma, 1989; Zucker and Shim, 2009), that can affect the seismic properties of the uppermost mantle (Reynard et al., 2010).

At low temperature ($T < 700$ °C) and moderate pressures ($P < 6$ GPa), orthoenstatite may transform to a $P2_1/c$ polymorph depending on stress and on the presence of H_2O in the system (Ulmer and Stalder, 2001). This polymorph transforms to a high-temperature $C2/c$ phase (Sharma, 1989), all being metastable in the pure $MgSiO_3$ system. The $P2_1/c$ polymorph is also observed as a quench phase of a high-pressure phase ($P > 6$ GPa), with a monoclinic ($C2/c$) clinoenstatite structure distinct from the high-temperature phase. First evidence of that phase was obtained from Raman spectroscopy at high pressure of a $MgSiO_3$ sample after laser heating in the DAC (Chopelas and Boehler, 1992). First principles calculations based on DFPT allowed the calculation of the phase boundary between $P2_1/c$ and $C2/c$ structures (Yu et al., 2010). Raman spectroscopy was used to follow the $P2_1/c$ to $C2/c$ transformation at high pressure in Fe-rich (Mg,Fe) SiO_3 pyroxenes (Ross and Reynard, 1999). Higher-pressure transformations have been observed by Raman spectroscopy (Lin, 2003, 2004; Zhang et al., 2013), and the structure of the high-pressure phase was refined in the $P2_1/c$ space group with yet a different structure than the low-pressure $P2_1/c$ polymorph (Zhang et al., 2012).

The complex polymorphism of enstatite is likely to be influenced by the chemical variations of pyroxenes in natural systems, including the substitution of iron and calcium for magnesium and aluminum for divalent cation and silicon. These effects remain largely unknown and could have significant effects on seismic properties because of the elastic softening associated with second-order transitions at high temperature.

2.09.3.6 Akimotoite and Majoritic Garnets

Akimotoite, the ilmenite-structured phase of (Mg,Fe) SiO_3 identified in natural meteorite samples (Tomioka and Fujino, 1999), was first synthesized as a solid solution with Al_2O_3 component under mantle high- P,T conditions (Liu, 1977). It is stable within a narrow high P range that could occur within cold subducted regions at 600–700 km depth toward the bottom of the transition zone, perhaps extending into the top of the lower mantle (Chen and Brudzinski, 2001; Gasparik, 1990; Ito and Yamada, 1982; Karki and Wentzcovich, 2002; Wentzcovich et al., 2004b).

The Raman spectrum is dominated by an intense peak at 799 cm^{-1} that was assigned by Ross and McMillan (1984) and McMillan and Ross (1987) as due to the A_g symmetric Si–O stretching mode of the octahedral SiO_6 groups in the structure. The vibrational spectra and elastic properties of $MgSiO_3$

ilmenite, or akimotoite, have been determined by Raman, IR, and Brillouin spectroscopies, including spectra obtained at high T and high P , and the lattice dynamics have been studied using both empirical simulations and first principles calculations (Chopelas, 1999; Hofmeister and Ito, 1992; Karki and Wentzcovich, 2002; Liu et al., 1994; McMillan and Ross, 1987; McMillan et al., 1996b; Reynard and Rubie, 1996; Ross and McMillan, 1984; Wall and Price, 1988; Weidner and Ito, 1985; Wentzcovich et al., 2004b).

In their high-pressure and high-temperature Raman spectroscopic study, Reynard and Rubie (1996) determined Grüneisen shifts and anharmonic parameters for the Raman-active modes. The experimental and theoretical results have been used to estimate the P,T Clapeyron slopes for the garnet-ilmenite and garnet-perovskite phase boundaries within the mantle (Chopelas, 1999; Hofmeister and Ito, 1992; McMillan and Ross, 1987; Reynard et al., 1996; Wentzcovich et al., 2004b). The entropy calculated from vibrational models has also been combined with calorimetric data to determine phase boundaries within the $MgSiO_3$ – Mg_2SiO_4 – SiO_2 system over the P,T range of the transition zone (Ashida et al., 1988).

A majoritic garnet based within the (Mg,Fe) SiO_3 system containing octahedrally coordinated Si^{4+} could also be present within the transition zone under high- T conditions, and like $MgSiO_3$ ilmenite, it could extend into the lower mantle (Akaogi and Akimoto, 1977; Akaogi et al., 1987; Kato, 1986; Kato and Kumazawa, 1985; Ringwood, 1967; Yusa et al., 1993). As with other high-density silicate mineral phases, majoritic garnet was identified and characterized in shocked meteorites (Coorara and Tenham), using a combination of optical microscopy, x-ray diffraction, and IR and Raman spectroscopies (Jeanloz, 1981; McMillan et al., 1989; Ringwood, 1967; Smith and Mason, 1970). x-Ray diffraction and vibrational spectroscopy of the end-member garnet $MgSiO_3$ indicate that the phase is tetragonally distorted (Akaogi et al., 1987; Kato and Kumazawa, 1985; McMillan et al., 1989). At high T and P , solid solutions exist between majorite and pyrope ($Mg_3Al_2Si_3O_{12}$) end-members. Members of the series have been studied by vibrational spectroscopy at high pressure (Liu et al., 1995).

The IR and Raman modes have been assigned (Geiger and Kolesov, 2002; Hofmeister and Chopelas, 1991a,b; Kolesov and Geiger, 1998, 2000; McMillan et al., 1996b) and used to construct model VDOS functions to predict the specific heat and entropy under high- P,T conditions (Geiger and Kolesov, 2002; Hofmeister and Chopelas, 1991a). The lattice dynamics and VDOS of the upper mantle garnets have now been determined using ionic model calculations combined with INS measurements (Artoli et al., 1996; Mittal et al., 2000, 2001; Pavese et al., 1998).

2.09.3.7 Aluminous Phases

Aluminous phases, and especially hollandite, may play a significant role in transporting large cations, like K and U, into the deep mantle. Silicate hollandites formed in shocked alkali feldspars have been observed by Raman spectroscopy in meteorites (Gillet et al., 2000a). They become stable around 300 km depth (Akaogi et al., 2004) and can persist up to very high pressures and temperatures (Hirao et al., 2008). In their structure, corner-sharing octahedra form tetragonal tunnels that

host the large cations. In some hollandite-type compounds, there is a mismatch between the size of the cations and the dimensions of the tunnels, resulting in the appearance of modulations. In case of the mantle silicate hollandites, the mismatch participates to the development of an elastic instability at high pressures. The instability has been observed experimentally (Boffa-Ballaran et al., 2009) and computed theoretically (Caracas and Boffa-Ballaran, 2010) and depends on the Na/K content. This dependence has been explicitly addressed in calculations that employed alchemical pseudopotentials, that is, linear combinations of the basis and projectors of elemental atomic pseudopotentials in the amount corresponding to the one present in the solid solution (Cohen, 2007). This approach allows studying the symmetry and properties of solid solutions and gives results in good agreement with the experiment (Caracas and Boffa-Ballaran, 2010).

The same methodology has been applied to compute the Raman spectra and elastic tensors of spinel, MgAl_2O_4 (Caracas and Banigan, 2009). Spinel has a rich phase diagram (Akaogi et al., 1999) with decompositions and recombinations under pressure (Catti, 2001). The cubic structure is stable up to about 15 GPa (Akaogi et al., 1999). Comparison between the computed (Caracas and Banigan, 2009) and the measured Raman spectra evidences Mg–Al disorder on the tetrahedral and octahedral sites (Slotznick and Shim, 2008).

2.09.3.8 OH in Mantle Minerals and Hydrous Phases

It has long been recognized that nominally anhydrous minerals such as olivine, pyroxene, and garnet can incorporate up to several tens to hundreds of ppm OH into their structure and that this could contribute substantially to the water budget of the mantle (Aines and Rossman, 1984a,b,c; Bell and Rossman, 1992; Rossman, 1996). These experimental determinations of OH incorporation into the mineral structure were made by IR spectroscopy. Solubilities and partitioning coefficients determined from spectroscopy are used to construct thermodynamic models (Ferot and Bolfan-Casanova, 2012; Keppler and Bolfan-Casanova, 2006). Some studies have explored the potential of Raman spectroscopy for dosing OH in minerals and glasses (Di Muro et al., 2006; Thomas et al., 2008). Wadsleyite and ringwoodite accept large quantities of H into its structure, perhaps even determining the overall water budget of the mantle (Downs, 1989; Kohlstedt et al., 1996; McMillan and Hofmeister, 1988; Smyth, 1987; Young et al., 1993). Deeper within the Earth, lower mantle minerals have been found to contain dissolved OH species in experimental runs carried out under high- P,T conditions but with overall solubilities lower than in upper mantle minerals (Bolfan-Casanova et al., 2000, 2002; Keppler and Bolfan-Casanova, 2006; Meade et al., 1994; Pawley et al., 1993).

Nominally anhydrous phases can incorporate significant amounts of the ‘water’ component, but the transfer of water from the surface down to the Earth’s mantle is achieved in cold subduction zones by minerals that contain nominally water molecules or OH groups, representing up to 15 wt% H_2O . Minerals like serpentine and lawsonite are major water carriers in ultramafic and mafic compositions, respectively. Both present displacive phase transitions at high pressure that were evidenced by x-ray diffraction and IR and Raman

spectroscopic studies (Auzende et al., 2004; Daniel et al., 1999, 2000; Nestola et al., 2010; Reynard and Wunder, 2006; Scott et al., 2007). Other dense hydrous phases resulting from the high-pressure transformation of serpentine, lawsonite, and other major hydrated minerals have been characterized by vibrational spectroscopy (Hofmeister et al., 1999; Koch-Müller et al., 2005). Attempts to combine vibrational spectroscopic data and first principles calculation of D/H substitution effects on the VDOS have yielded prediction of hydrogen isotopic fractionation between hydrous minerals and water (Méheut et al., 2007, 2010; Reynard and Caracas, 2009) that are useful for choosing among contradictory experiment results due to sluggish reaction rates at low temperatures.

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2.10 Multi-Anvil Cells and High Pressure Experimental Methods

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2.10.1 Introduction

2.10.1.1 Beginning of High-Pressure Earth Science

Since the Greek philosopher Aristotle pointed out, in the fourth century BC, that the Earth had a spherical shape, the state of the inside of the Earth must have been a fantastic and baffling question for human beings. In the early twentieth century, the Earth's interior became an object of scientific research as a result of the information provided by seismology. [Jeffreys \(1939\)](#) and [Gutenberg \(1948, 1951\)](#) constructed the models showing the distribution of seismic velocities over the entire solid Earth from the surface to the center. The solid Earth was divided into the crust, the mantle, and the core with increasing depth, based on marked changes in seismic velocities. These works made it possible to model the density and

thereby the pressure within the Earth as functions of depth ([Bullen, 1937](#)). It was shown that the conditions of pressure up to 360 GPa and temperatures up to presumably several thousand Kelvin were extended into the Earth's interior. In order to decipher such Earth models in terms of material science, therefore, high-pressure and high-temperature experiments on deep-Earth materials should be carried out to reveal what structures and properties they possess under the corresponding conditions. The research processes used to reveal the constitution and state of the Earth's interior by combining the seismology-based knowledge and the results of high-pressure studies may be referred to as 'high pressure Earth science.'

The embryo of the high-pressure geosciences would ascend to [Bernal's \(1936\)](#) prophesy that discontinuous increases in seismic velocities at a depth of approximately 400 km, found

by Jeffreys, would be caused by the transformation of common olivine to a new phase possessing the spinel structure. It is interesting to note that, as a crystallographer, Bernal knew about the olivine-spinel transformation Mg_2GeO_4 undergoes at atmospheric pressure. Later, Birch (1952) examined the homogeneity of the Earth's interior by analyzing the seismic models of Jeffreys (1939) and Gutenberg (1948, 1951) using the equation of state based on the finite strain theory. Birch concluded that the layer B (Bullen's nomenclature, depths of 33–413 km in the mantle) was composed of olivine, pyroxenes, and garnet, whereas the layer D (depths of 984–2898 km) was composed of close-packed oxides of magnesium, silicon, and iron, similar in structure to corundum, rutile, or spinel. The intermediate layer C was characterized as a layer of transition from the familiar silicate minerals in layer B to the high-pressure phases in layer D. Birch also pointed out that the outer core was interpreted as liquid iron alloyed with a small fraction of lighter elements and the inner core as crystalline iron. Birch's argument was so concrete and convincing that many developed a desire to substantiate his conclusions using high-pressure experiments.

Birch's prediction was soon supported by high-pressure syntheses of the spinel type of Fe_2SiO_4 by Ringwood (1958) and the rutile type of SiO_2 (stishovite) by Stishov and Popova (1962). The special importance of the latter work should be noted because it was verified that the Si^{4+} ion could be accommodated in the six-fold coordinated site with respect to the oxide ion at high pressure. It was certainly remarked that the most important effort in high pressure Earth science in the 1960s was construction of a phase diagram of the system $\text{Mg}_2\text{SiO}_4\text{--Fe}_2\text{SiO}_4$ focusing on clarification of the 410 km seismic discontinuity (see Chapter 2.21). This work was carried out actively by both Ringwood's group of ANU (Ringwood and Major, 1970) and Akimoto's group (Akimoto and Fujisawa, 1968) of ISSP, University of Tokyo, somewhat competitively. Reviewing the process of the research would be very instructive: the stability field of the spinel (γ) phase was expanded to a richer-in- Mg_2SiO_4 component according to improvement of the high pressure devices. High pressure phase relations of many analogous compounds, such as germinates, titanates, and stanates, were widely studied with crystal chemical implications. In the course of the research, it was found that a new phase called modified spinel (β) emerged in compositions close to the Mg_2SiO_4 end member, and it has a stability field between those of olivine (α) and spinel (γ). Based on the phase diagram of the system $\text{Mg}_2\text{SiO}_4\text{--Fe}_2\text{SiO}_4$, it was proposed that the 410 km discontinuity would be responsible for a series of transformations, $\alpha \rightarrow (\alpha + \gamma) \rightarrow (\alpha + \beta) \rightarrow \beta$, of the mantle olivine with a composition close to $(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$ (Akimoto et al., 1976; Ringwood, 1970).

In spite of such epoch-making achievements by both groups, the binary loop of ($\beta + \gamma$) did not reach to the end member Mg_2SiO_4 because of the limitation of attainable pressures of the high-pressure apparatuses adopted (the Bridgman anvil by ANU and the tetrahedral anvil press by the ISSP). Nevertheless, it was strongly recognized that performance of the adopted apparatus was crucial to acquire excellent results and thus to promote our knowledge about the Earth's interior. Therefore, many attempts to make novel high-pressure apparatuses and also to improve the existing apparatus were made

in the late 1960s–70s. Major goals of the decade were the synthesis of $\gamma\text{-Mg}_2\text{SiO}_4$ and further understanding of the post-spinel, the transformation of the spinel phase at still higher pressures. As a consequence, two devices possessing characteristics complementary to each other, the multi-anvil apparatus (MAA) and the diamond anvil cell (DAC), were developed in this period and have been fundamental in the process of the high-pressure Earth sciences in subsequent years (see Chapter 2.11). Actually, $\gamma\text{-Mg}_2\text{SiO}_4$ was successfully synthesized by Suito (1972) using the MAA, and the decomposition of $\gamma\text{-Fe}_2\text{SiO}_4$ into an oxide mixture of FeO wüstite and SiO_2 stishovite was found by Mao and Bell (1971) employing the DAC.

This chapter explains the mechanical structure of multi-anvil types of high-pressure apparatuses and provides brief reviews of their development and a description of their applications to high-pressure Earth science. The MAAs which have been in practical applications so far are classified into the tetrahedral, cubic, and octahedral types, corresponding to the number of anvils (4, 6, or 8), and the corresponding shapes of the sample chamber (tetrahedron, cube, and octahedron, respectively). As the octahedral type has been the most widely adopted in the last few decades, descriptions will be focused on this type of apparatus.

2.10.1.2 Opposed Type High-Pressure Apparatuses and Principles of High-Pressure Design

Because the MAA was developed based on the summarization of faults and limitations of the piston-cylinder and the uniaxial opposed type apparatuses that already existed, a brief review of these classical types of apparatuses may be useful in understanding the structural concept of the MAA. In this context, Bundy (1962) described the general principles of high-pressure apparatus design by reviewing the various types of existing apparatuses. By applying these principles it becomes possible to generate pressure higher than the yielding and/or fracture strength of materials which are used to build up the high pressure chamber. The important principles are as follows.

2.10.1.2.1 Pre-compression

In the piston-cylinder apparatus, a cylindrical sample assembly with a diameter of 10–20 mm is set in a bore space of a thick-walled cylinder and compressed by inserting a piston with the aid of a uniaxial press as schematically shown in Figure 1. The ratio of the inner to outer diameter of the cylinder is usually around 10. On loading pressure, the maximum hoop tensile stress emerges at the inner wall of the bore, which depends on the ratio but is definitely higher than the applied bore pressure within the elastic limit. Therefore, the attainable pressure must be less than the tensile strength of the bore material. In order to surpass this limitation, the central core is kept in a high compression state at zero loading so that the hoop tension at bore wall is still less than the tensile strength of the material when the bore pressure is applied. This situation is usually realized by thrusting a few coaxial cylinders, whose outer diameter is slightly larger than the inner diameter of the next outer cylinder, into a single cylinder. Using this method, the maximum loading pressure could rise nearly to the sum of the

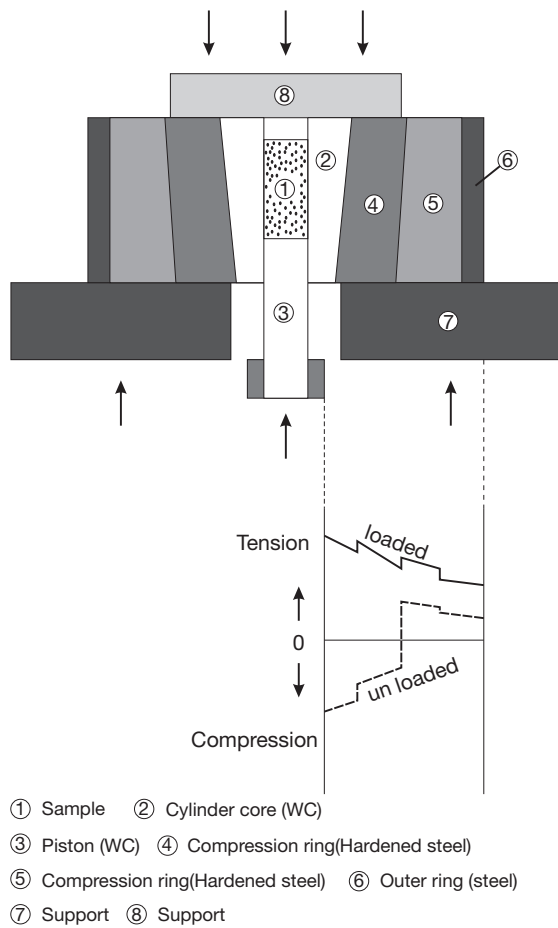


Figure 1 A cross section of the piston-cylinder apparatus. The inner core of WC and the middle rings are in pre-compression, so that the tensile stress inside the core may not exceed the tensile strength of WC on loading.

compressive and tensile strengths of the bore material. The piston-cylinder apparatus is now widely adopted in experiments up to pressures ca. 5 GPa because of the large sample volume and the performance of precise temperature control.

2.10.1.2.2 Massive support

One of the simplest high pressure apparatuses is an array of truncated conical pistons with a flat face at the top as shown in Figure 2, which was developed by Bridgman in 1952 and is called the Bridgman anvil. Bundy regarded this device as a MAA with two pistons. A thin disc sample surrounded by a pyrophyllite gasket is compressed between the flat faces of the pistons and the pressure is sustained by the pinched gasket. The tungsten carbide (WC) pistons are gripped by hardened steel rings under high hoop tension so that the pistons are under compression and slight elongation. Because the top surface area of the piston is around a tenth of the cross sectional area of the body of the piston, the high compressive stress of the surface top is dispersed backward rapidly without breakage occurring. Apparatuses of this type work easily at higher than 10 GPa, which is more than twice the compressive strength of WC. This design concept is called 'principle of

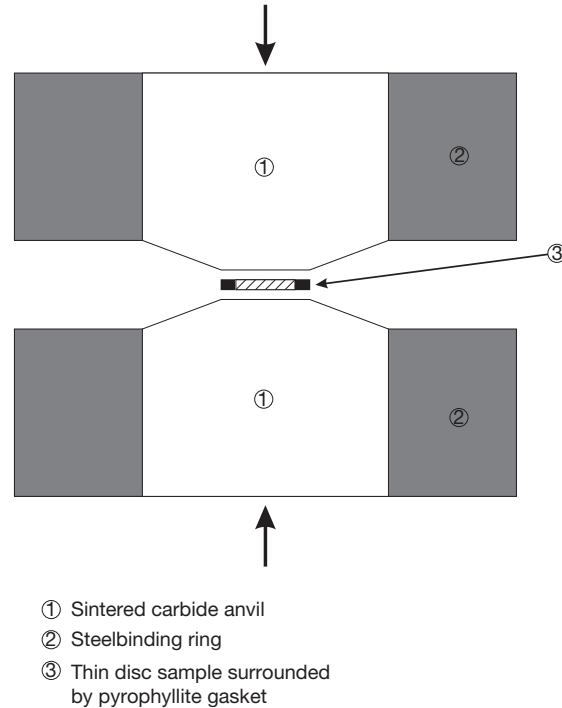
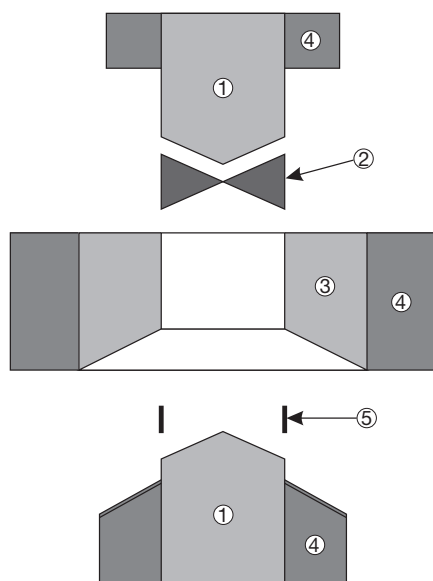


Figure 2 A cross section of the Bridgman anvil (see text). Ringwood's research on the olivine-spinel transformation was carried out by using this apparatus (Ringwood and Major, 1970).

massive support,' and has been an important criterion in the design of MAAs. Ringwood (1970) carried out high-temperature experiments by inserting a thin resistance heating element with the sample between the anvil faces. It should be mentioned that the DAC is regarded as an evolved apparatus from the Bridgman anvil as it adopted the hardest material, diamond.

2.10.1.2.3 Lateral support

Drikamer and Balchan (1962) extensively raised the attainable pressure of the Bridgman anvil-type apparatus by supporting the tapered lateral area of the piston with a pyrophyllite pellet as illustrated in Figure 3. This apparatus, the Drikamer cell, was mostly used for measuring electric resistance of metal at room temperature or low temperatures. By using work-hardened WC as the piston, the maximum pressure reached nominally higher than 50 GPa. The important role of the lateral support in high pressure generation is demonstrated in the belt apparatus, a cross section of which is schematically drawn in Figure 4. Two opposed pistons compress a sample retained in a strongly reinforced multi-layered cylinder, or belt, in a uniaxial press. The principle of massive support is utilized in both the conically shaped pistons and the cylinder. In addition, both the piston and the cylinder are circumferentially supported by the compressible conical gasket made of laminated pyrophyllite-and-metal. The gasket not only prevents extrusion of the materials inside the chamber but also makes the pressure gradient along the flanks of the piston and cylinder gentle, preventing them from breaking. Therefore, the belt apparatus and similar apparatuses can produce pressures



- ① WC piston ② Pyrophyllite pellet
- ③ WC cell ④ Steel outer jacket
- ⑤ Mica insulating sleeve

Figure 3 A cross section of the Drickamer cell (see text).

higher than 10 GPa over a large volume and have been used most popularly in the industrial field, such as in diamond synthesis.

2.10.1.3 Conceptual Advantages of the MAAs over the Opposed Anvil Apparatuses

MAAs with 4 or more anvils were invented in the period between the late 1950s and the 1960s. It is absolutely true that the volume of a three-dimensional sample chamber is intrinsically larger than those of the anvil apparatuses with two-dimensional sample spaces, such as the Bridgman anvil and the Drickamer cell. Another merit of the MAAs is that the stress states in the samples are much closer to hydrostatic despite the usage of a solid pressure medium due to compression from multi-directions as schematically shown in Figure 5.

When all the anvils are put together, anvil tops form a polyhedral space at the center. The polyhedral pressure medium, with or without a pre-gasket, is set at the central polyhedral hollow space. As the anvil of the MAA has the shape of truncated pyramid, it is clear that the anvil is in massive support when the truncated top face compresses the central polyhedral pressure medium. The generated pressure is sustained by the friction of the gasket which is caused by strong compression between the flanks of the neighboring anvils. In other words, the anvil is under the lateral support. It is important to point out that all the forces applied to the anvil are compression, which suggests a potential for the MAA to generate high pressures. Actually, the MAAs equipped with a WC anvil can generate pressures higher than the piston-cylinder and belt apparatuses equipped with WC. This is because the

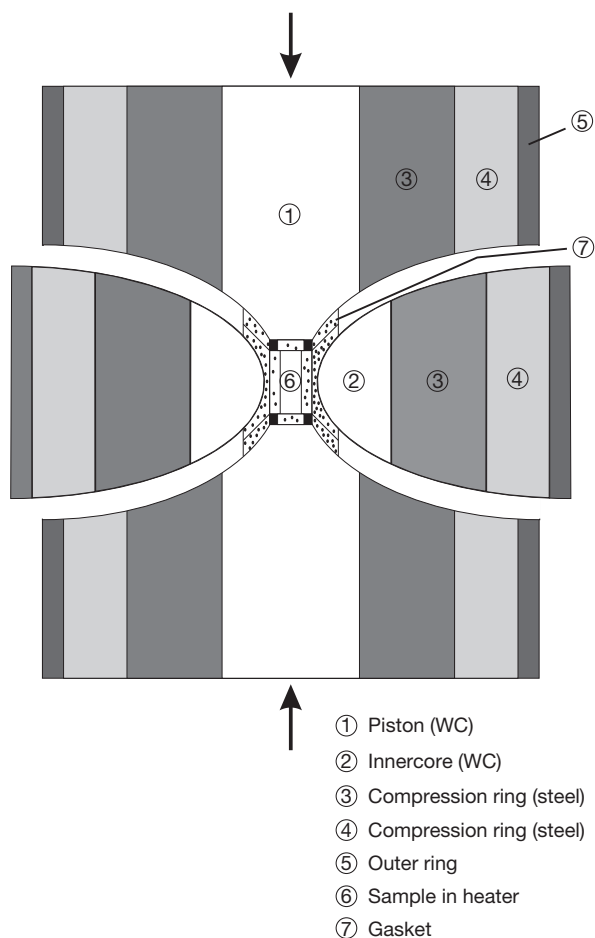


Figure 4 A cross section of the belt apparatus (see text).

hoop tensile stress at the inside walls of the bore is the critical factor to determine the maximum attainable pressure in the latter apparatuses.

2.10.2 Multi-anvil Apparatuses

As mentioned earlier, the MAAs in practical applications have been the tetrahedral, cubic, and octahedral types, corresponding to the number of anvils, 4, 6, and 8, respectively. A polyhedral pressure medium larger than the space usually is set with compressive and insulating gaskets in gaps between the flanks of adjacent anvils. On thrusting the anvils to the center, the central pressure medium is squeezed to generate high pressure there. The generated pressure is confined by the compressed gasket (which is formed of the preset gasket and the extruded pressure medium) into the gaps. It is true that, in many MAAs, more than 90% of the applied force is balanced with compression of the gasket.

For further increased surface numbers, the regular polyhedral sample chamber changes to a dodecahedron with 12 anvils and to an icosahedron with 20 anvils. With the increasing number of anvils, the ratio of stroke of the anvil to shrinkage of the anvil gap increases and so the sample is more effectively compressed and the hydrostaticity of the solid pressure medium

becomes higher. However, the solid angle of the anvil from the apex becomes smaller, which makes the massive support less efficient. A trial of the icosahedral compression carried out at Kawai's laboratory at Osaka University in the late 1960s resulted in breakage of many anvils. Another problem with such MAA is an inherent difficulty in aligning the anvils at the initial setting and also during compression. To my knowledge, the octahedral compression has the largest number of anvils in practice and displays the best compromise between the number of anvils and the massive support.

As the pressure in the MAA is confined by the compressed gasket between flanks of adjacent anvils, the generated pressure is sustained in subtle balance with the friction of the gaskets. Therefore, the slight unbalance due to an abrupt change of thrusting force or flow-out of the medium causes an explosive extrusion of large amounts of the pressure medium into the gaps with a big characteristic sound. This phenomenon has been called blow-out and it frequently causes serious damage to the anvils. There is a large hysteresis between compression and decompression trajectories in the relationship of generated pressure versus applied load. The blow-out is likely to occur in the later stage of decompression where the pressure decreases the most rapidly with decreasing load. It is quite certain that the higher the internal friction of the pressure medium, the higher the probability of occurrence of blow-out.

Three types of methods are adopted to drive anvils of the MAAs: (1) Each anvil is driven by an individual ram which is fixed to a solid frame. (2) In order to ensure uniform compression, the whole anvil system is immersed in a fluid

(oil or water) chamber and is thrust with the aid of hydrostatic pressure in the chamber. (3) An assembly of anvils is squeezed between a pair of solid guide blocks which is driven by a uniaxial hydraulic press.

In this section the tetrahedral, cubic, and octahedral apparatuses will be reviewed successively.

2.10.2.1 Types of MAAs

2.10.2.1.1 Hall's tetrahedral apparatus

The first MAA was Hall's tetrahedral apparatus (1958) in which four faces of tetrahedral pressure medium are simultaneously compressed by four WC anvils with equilateral triangular faces. Pyrophyllite was mostly adopted as the pressure medium. Each anvil is driven by a hydraulic ram which is fixed at a corner of a rigid tetrahedral frame pointing inward as shown in [Figure 6](#). The edge length of the pressure medium is larger than the edge length of the anvil faces. Therefore, on compression, part of the pyrophyllite medium is extruded into the gap between the side faces of the anvils to form the gasket which confines the generated pressure. The maximum attainable pressure was approximately 12 GPa at room temperature.

It is interesting to note here that the tetrahedral apparatus was interfaced with the x-ray diffraction system by [Hall et al. \(1964\)](#) (see [Section 2.10.4.1](#)). The tetrahedral apparatus generally has not been used for the last three decades. However, this apparatus initiated the development of MAAs and their versatile abilities for material synthesis and in situ x-ray observation.

2.10.2.1.2 Cubic anvil apparatuses

The von Platen's cubic apparatus was probably the first apparatus to compress a cubic pressure medium using six identical anvils along three paths perpendicular to each other. The six anvils form the shape of a split sphere with a truncated square surface at the top and a spherical back surface. The six-anvil assembly, covered by a spherical copper sheath, was put into a cylindrical water reservoir and the cubic sample assembly was compressed with the aid of the water pressure in the reservoir. The whole cross section of the apparatus is diagrammatically

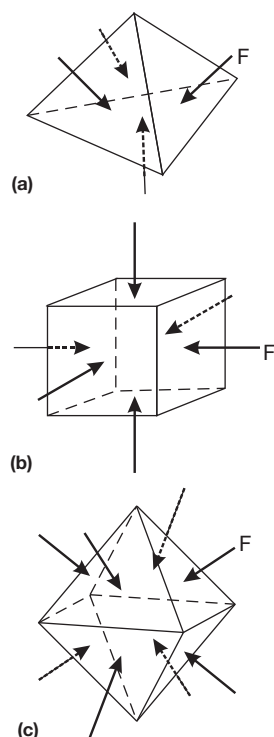


Figure 5 Conceptual drawings for compression of the polyhedral pressure media. All surfaces of the regular polyhedra are thrust by equivalent normal forces. (a), (b), and (c) show the tetrahedral, cubic, and octahedral compression, respectively.



Figure 6 Photo of the Hall's tetrahedral anvil apparatus. This apparatus was used in the research of the olivine-spinel transformation in the 1960s by Akimoto's group ([Akimoto and Fujisawa, 1968](#)).

shown in Figure 11 in Bundy (1962). The apparatus was mainly employed to make artificial diamonds.

A cubic apparatus in which six anvils are driven by a uniaxial press by means of a set of rigid upper and lower guide blocks was first developed in a collaboration between Kyoto University and Kobe Steel Co. in the mid-1960s. The cross section of the apparatus recently designed is schematically drawn in Figure 7 and shows the central cubic space filled with the Kawai-cell (Section 2.10.2.1.3). The cubic pressure medium is compressed synchronously by the six WC anvils. The upper and lower surfaces of the cube are thrust by the upper and lower anvils fixed to the guide blocks, and four side surfaces are thrust by the anvils that are forced to proceed to the center by sliding between the back surfaces of the anvil supports and inner surfaces of the guide blocks. By utilizing a 500 ton ($1 \text{ ton} = 10^{-2} \text{ MN}$) press, pressures up to 10 GPa can be generated over a volume of 1 cm^3 . This apparatus is called the DIA-type apparatus because the cross section of the anvil support resembles that of a Brillouin-cut diamond. It should be noted that in situ x-ray observation at high pressures and simultaneously at high temperatures was first carried out employing this apparatus (Inoue and Asada, 1973).

Cubic anvil apparatuses in which each anvil is backed up by a hydraulic ram as in the Hall's tetrahedral apparatus were also developed in several laboratories (e.g., Shimada, 2000). Six independently moving rams of several MN are fixed to a steel frame along the three principal directions. The movement of each ram is measured by the linear variable differential transformer. Advances of the six rams are regulated by an oil pressure in the pumping system which is semi-manually controlled. As the ram can be driven in a mutually independent manner, this machine has mainly been adopted in the study of deformation of rocks under confining pressure (Shimada, 1981).

Application of the MAA to the rheological study of mantle materials was developed by modifying the DIA-type apparatus to the deformation DIA (D-DIA) by Wang et al. (2003). In this apparatus, the upper and lower anvils are connected to the differential rams mounted inside the guide blocks. Therefore,

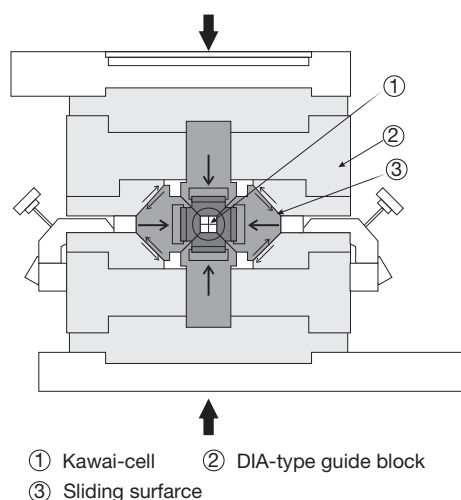


Figure 7 The DIA-type guide block compressing the Kawai-cell (see text). There is friction between the inner surfaces of the guide block and the outer surfaces of the anvil support.

extra deviatoric stress can be applied to the sample by the rams, in addition to confining the pressure produced by the main jack. By combining the D-DIA with synchrotron x-ray, the corresponding axial strain is precisely measured by x-ray imaging together with in situ pressure determined by compression of standard material (see Section 2.10.4). This device broke new ground in the rheology field of high-pressure mineral physics.

2.10.2.1.3 Octahedral anvil apparatus

Development of an octahedral anvil apparatus, called the Kawai-type apparatus, in which an octahedral pressure medium was compressed by eight equivalent WC anvils started in the middle of the 1960s under the direction of the late N. Kawai at Osaka University (Kawai, 1966). Traces of the technological development have been summarized by Ito et al. (2005) and are schematically illustrated in Figure 8 (Kawai, 1966; Kawai and Endo, 1970). A WC sphere was split into eight identical blocks by three planes mutually perpendicular and crossing at the center. After truncation of the top to form a regular triangle, the eight split-sphere anvils were reconstructed with an octahedral pressure medium and adjacent gaskets at the center, and covered with a rubber capsule to be compressed in a cylindrical oil chamber (Figure 8(a); Kawai, 1966). Therefore, the concept is similar to von Platen's cubic apparatus but the whole apparatus was greatly simplified and without a cooling system.

With the enlargement to generate higher pressure, the system evolved to the double-staged, split-sphere system (Kawai and Endo 1970) shown in Figure 8(c) via an intermediate stage shown in Figure 8(b). The assembly of eight cubic anvils of WC with the octahedral pressure medium and gaskets, the Kawai-cell, is squeezed by the six first-stage anvils made of hardened steel with the square top surface and the cubic split-sphere-shaped back surface. The whole assemblage of the first and the second anvils is compressed by the oil pressure outside the rubber capsule. It should be noted that versatility of the apparatus was remarkably increased by adopting a disposable cubic WC anvil that is much easier to machine than a split sphere. For example, a WC cube can be used for multiple purposes by truncating the different corners in different sizes: for example, smaller for higher pressure and larger for bigger sample volume experiments.

Three of the six first-stage anvils were later glued together in a hemispheric cavity of a steel vessel to form a guide block, and the two guide blocks were aligned in a hydraulic press so that the cubic Kawai-cell was compressed by the uniaxial force along the $[111]$ direction (Kawai et al., 1973). The guide block and the 5000 tons press USSA 5000, installed at the Institute Study of the Earth's Interior (ISEI), Okayama University are shown in Figure 9. In this system, a good match of the spherical surfaces of the anvil back and the cavity of the vessel is very crucial to squeeze the Kawai-cell to high tonnages. Ohtani et al. (1987) avoided the situation by adopting a set of split-cylinder wedges which was fixed to a bolster plate and supported by a massive cylinder of hardened steel. The split-cylinder system was modified by Walker et al. (1990) to an assembly comprised of an unanchored cylindrical cluster of removable wedges set in loose supporting rings which accommodate appreciable strain under loading. The height to

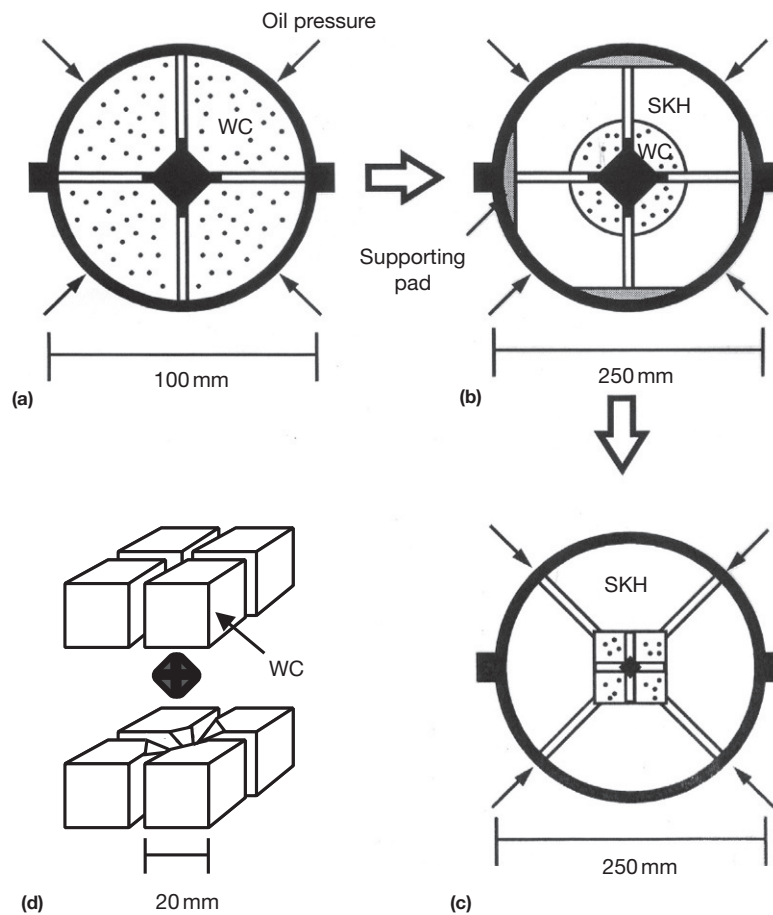


Figure 8 Evolution of the Kawai-type high-pressure apparatus. (a) An eight split sphere assembly of WC covered by a rubber capsule is compressed in an oil chamber. (b) On enlargement, six supporting pads are placed at junctions of the assembled split spheres to keep the whole sphere in the perfect shape under compression. (c) The supporting pads turn into six outer split-sphere assemblies, and the inner split blocks to inner cubic anvils. (d) The Kawai-cell composed of 8 cubic anvils and an octahedral pressure medium.

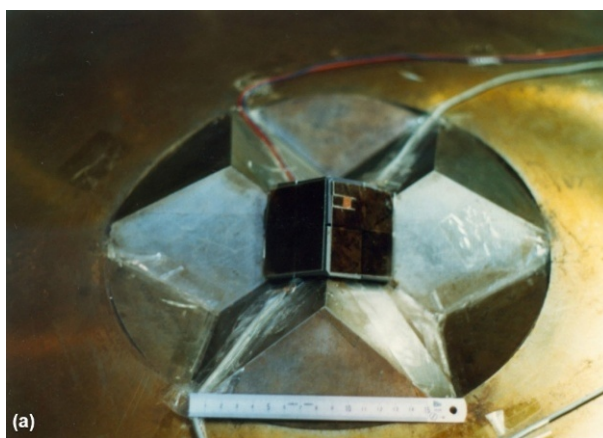


Figure 9 Photos of Kawai-type pressure apparatus installed at ISEI, Okayama University. (a) Lower half of the guide block made up of three bound split spheres. The Kawai-cell covered by mica sheets is set at the center. (b) A 5000 ton press to drive the split-sphere guide blocks.

diameter of the cylindrical cluster wedges was chosen so that the cubic cavity formed by them does not have angular relationships distorted under appreciable strain.

2.10.2.1.4 Combination of multi-anvil systems

A double-stage, split-sphere apparatus meant to compress a cubic or tetragonal sample chamber was developed at the Institute of Mineralogy and Petrology, Siberian Branch of the Russian Academy of Science, Novosibirsk, Russia under the direction of the late I. Y. Malinovskiy. A photo of the apparatus is shown in [Figure 10](#). An assembly of eight steel anvils with a split-sphere shape is held in a spherical cavity of the high pressure vessel divided into upper and lower parts which is supported by half couplings. The top of the split-sphere anvil is truncated so that an octahedral space is formed at the center when the eight are assembled as the Kawai-type apparatus. Six WC wedges are put with the cubic or tetragonal pressure medium, and the split-sphere anvil assembly is compressed by hydraulic pressure from outside of the rubber jacket surrounding the split sphere. The apparatus has actively been used in studies on formation and growth of diamonds ([Pal'yanov et al., 2002](#) and references listed therein).

Recently, the Kawai-cell has commonly been set in a cubic space of the DIA apparatus and squeezed by a uniaxial press. As the combination of both devices is the most feasible for x-ray optics, this has been set up in many facilities for high pressure x-ray experiments using the synchrotron radiation. In this case, however, force applied to the square surface of the Kawai-cell in this system is $1/3$ times the applied press load, compared with $1/\sqrt{3}$ times in the case of compression by the uniaxial force in the $[111]$ direction. It is known that friction on the sliding surfaces of the anvil supports and the guide blocks in the DIA apparatus usually loses 10–20% of the applied load (see [Figure 7](#)). Moreover, a discontinuous slip happens there instead of smooth sliding, which frequently causes the brown-out of the specimen in the Kawai-cell. In the DIA apparatus, the elastic deformation of the guide block is not uniform in the axial and lateral directions, thus it does not keep the sample chamber exactly cubic.

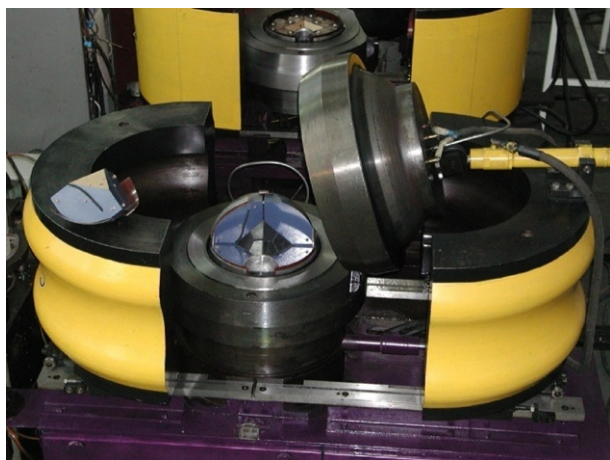


Figure 10 Photo of the double-stage, split-sphere apparatus developed at Institute of Mineralogy and Petrology, Siberian Branch of the Russian Academy of Science, Novosibirsk, Russia (see text).

2.10.2.1.5 The 6-axis apparatus

All the shortcomings of the DIA-type apparatus on squeezing the Kawai-cell could, in principle, be overcome by driving the six anvils with independently controlled rams (e.g., Shimada, 2000). In all such cubic apparatuses, the thrust force and progress of each ram are controlled manually by operating valves of the oil circuit as in [Hall's \(1958\)](#) tetrahedral apparatus. However, recent high-tech servomechanisms make it possible to adjust each anvil load within 10 kN and to synchronize the anvil advances within a few μm . Recently, a new 6-axis apparatus, HACTO-6, which satisfies these criteria was installed at our laboratory ([Ito et al., 2009](#)). Photos of the apparatus are shown in [Figure 11](#). Pressure generation using the Kawai-cell equipped with sintered diamond cubes (see [Section 2.10.2.2](#)) was carried out up to 60 GPa using pressure-fixed points of GaP, Zr, and Fe_2O_3 (see [Section 2.10.2.4](#)). The results were compared with those obtained by means of in situ x-ray observation (see [Section 2.10.4.4](#)) compressing the Kawai-cell of almost identical setup in the DIA apparatus. It was demonstrated that a significant amount of the applied load is lost by friction in the

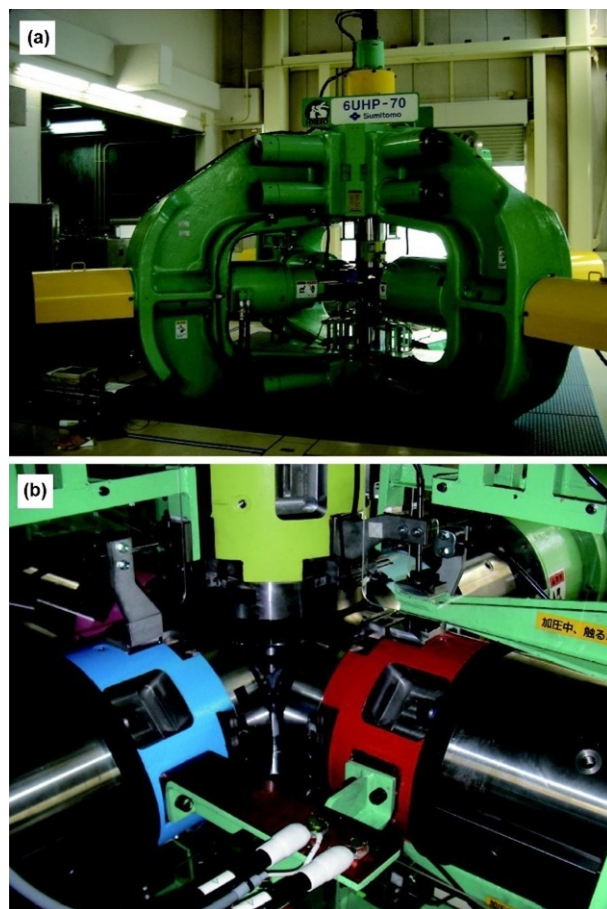


Figure 11 Photo of the 6-axis apparatus installed at ISEI, Okayama University (HACTO-6). The apparatus consists of a steel frame and six jacks whose actions are perpendicular to each other. (a) A full view of the frame and jacks. (b) The 6-axis and anvil tops put together at the center of the frame. The Kawai-cell is set at the cubic space formed by the anvil tops.

latter. The load loss increases with increasing load, or pressure, and amounts to 45% at ca. 60 GPa.

It may be important to point out that the 6-axis apparatus has a capability to perform deformation experiments under high confining pressure by compressing a cubic specimen instead of the Kawai-cell (Shimada, 2000) just like the D-DIA. As all the ball screw systems are driven independently in a precision less than 1 μm , the deformation experiments can be carried out under a precisely controlled strain rate with the specified deviatoric stress by adopting suitable software to drive the servo mechanisms.

Recently, similar 6-axis apparatuses have successively been installed at Bayerisches Geoinstitut, Germany (Manthilake et al., 2012) and JAEA/J-PARC center, Japan (Sano et al. 2012).

2.10.2.2 Anvil Materials

Let us consider a homogeneous solid material in the stress field that is specified by principal stresses σ_1 , σ_2 , and σ_3 . According to von Mises' theory of the maximum shear stress, the critical condition for the material to commence plastic flow is given as

$$(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2 = 2\sigma_e^2 \quad [1]$$

where σ_e is the uniaxial compressive strength of the material. Equation [1] indicates that, in order to generate high pressure without plastic deformation or fracture of an anvil, minimization of the left side and/or maximization of the right side are prime requirements. The former requirement demands the avoidance of the stress concentration on the anvil by selecting the pressure medium and the gasket of appropriate materials together with their suitable sizes. The latter, on the other hand, simply demands the use of the hardest material for an anvil.

WC has been the most commonly used material for anvils of the MAA. WC as a super hard alloy is sintered material of fine-grained, intermetallic compound WC with a small amount of Co as a binding agency. Mechanical properties of the WC alloy strongly depend on the amount of Co binder as shown in Figure 12. Compressive strength increases from 350

to 600 kgf m^{-2} with a decrease in Co content from 25 to 3 wt %, whereas tensile strength decreases from 150 to less than 50 kgf m^{-2} in the same variation of the Co content. Grain size of WC particles is also an important factor in controlling the toughness of the WC alloy. Recently, WC alloys possessing compressive strength greater than 700 kgf m^{-2} have been developed, with particle sizes are less than 5 μm . The maximum attainable pressure in the Kawai-type apparatus using WC has been limited to ca. 28 GPa (Kubo and Akaogi, 2000) over a volume of ca. 2 mm^3 , but quite recently it has been raised to 41 GPa (Katsura et al., unpublished data) by using a newly invented WC alloy.

The generated pressure using the Kawai-type apparatus has largely been extended by employing sintered diamond (SD) for anvil material since the late 1980s (e.g., Kondo et al., 1993; Ohtani et al., 1989). The SD is a composite of diamond and Co metal sintered in a similar mechanism to that for WC alloy. Mechanical properties of SD depend on the grain size of the sintered diamond particles. Although detailed information is not available, a lump of SD with a grain size typically less than 10 μm seems to be tougher than one with a larger grain and is suitable for anvil material. As the sintering conditions of SD is within the stability field of diamond (e.g., 4.5 GPa and 1500 $^\circ\text{C}$) however, available size of the cubic anvil of SD is at present limited to an edge length of 20 mm. The high level of hardness of SD, on the other hand, makes it difficult to machine SD cubes by polishing. These situations cause the costs of SD cubic anvils to be extraordinarily high compared to WC. The finished 20 mm SD cube costs approximately US\$ 8000. Consequently, the 14 mm cube, with a cost of approximately US\$ 2000, has remained the most practical to use. It is not possible to directly measure the compressive strength of super hard materials such as WC and SD, but hardness is a good measure with which to assess it. The Noop hardness of SD is ca. 49 GPa, about twice that of WC (Sung and Sung, 1966). In this context, eqn [1] suggests that much higher pressure can be generated using SD anvils than WC anvils.

Pressure calibration curves constructed based on the fixed points (see Section 2.10.2.4) are comparatively reproduced for the cases using SD and WC cubic anvils in the Kawai-type apparatus in Figure 13. The curves of SD were obtained using cubes with 14 mm edge lengths and 1.5 and 2.0 mm truncations, and that of WC was for cubes with 2.0 mm truncation. The difference in pressure efficiency between SD and WD is dramatic. It is suggested that the pressure generates almost linearly against load even at higher than 30 Pa in the SD anvil whereas generated pressure is saturated at around 20 GPa in the WC anvil.

Another type of diamond composite was invented by a research group of ANU (Ringwood et al., 1989). The composite is produced at pressures slightly lower than the diamond stability field using a SiC binder. Recently, a similar diamond/SiC composite has been synthesized in a cubic shape by a hot isostatic pressing (HIP) processing (Shimono et al., 2003). It is remarkable that the HIP conditions are at 1450 $^\circ\text{C}$ and 200 MPa for 30 min which are by far easier to produce than those within or close to the stability field of diamond. Recently Ohtaka et al. (2005) have proved the HIP processed diamond composite to be hard enough for generation of pressures up to 30 GPa using 10 mm cubes with truncated edge length 1.5 mm. It is certain

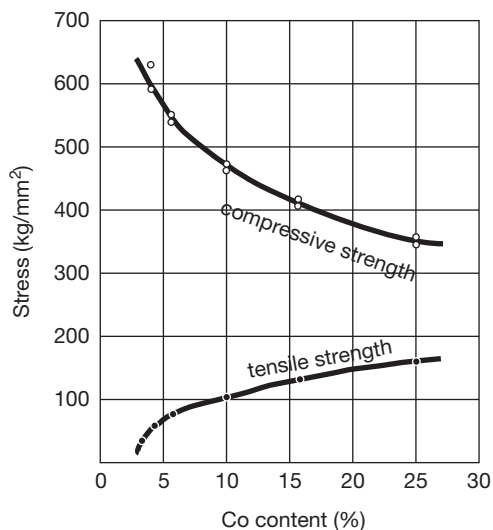


Figure 12 Mechanical properties of WC. Compressive strength (upper) and tensile strength (lower) are shown as a function of the Co content.

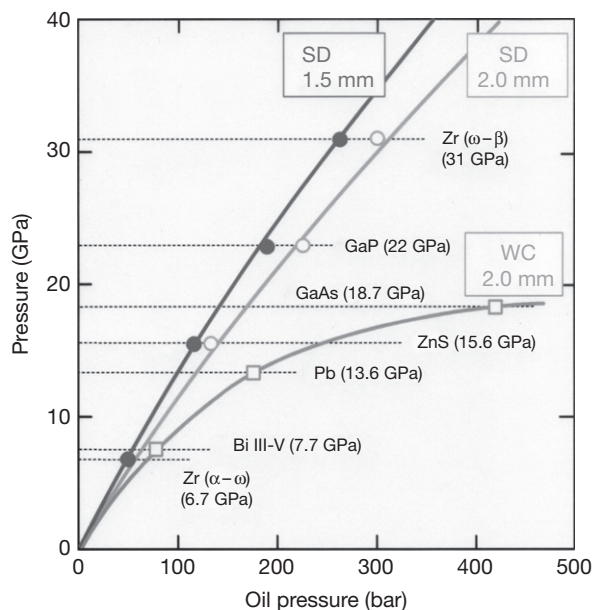


Figure 13 Pressure calibration based on the pressure fixed points. Curves of SD are obtained using cubes with 14 mm edge length and 1.5 and 2.0 mm truncations and that of WC is for 32 mm edge length and 2.0 mm truncation (see text).

that the HIP method supplies the composite at a much lower price than the composites sintered at high pressure. Hardness of the diamond/SiC composite is believed to be slightly lower than that of the diamond/Co composite. However, an important characteristic of the former is its low absorbency for x-ray, which makes it possible to use the anvils as the windows for versatile in situ x-ray observations such as radiography.

Boron nitride (BN) exhibits very similar properties to carbon. Cubic BN (cBN) possessing the zinc blend structure is stabilized under the almost identical P-T conditions where diamond is stable. In cBN, B and N are bound to each other by the covalent bond just like diamond, and the hardness of cBN is second to diamond. Therefore, sintered cBN is a suitable material for anvils of MAAs. A remarkable feature of cBN is also the low absorbency for x-rays. Recently, cubes of cBN with edge lengths up to 20 mm have become commercially available.

2.10.2.3 Pressure Media and Gasket Materials

The following properties are required for pressure medium of the MAA: (1) low internal friction to keep the sample in a high hydrostatic state, (2) low compressibility to raise pressure effectively, (3) low thermal conductivity, (4) very low electric conductivity, (5) high melting point which increases with pressure, (6) chemical inertia, and (7) stability at high temperature and high pressure. In addition to the above requirements, in a specified experiment such as in situ x-ray observation, high transparency of x-ray is crucial. As some of these requirements contradict each other, material should properly be selected according to the purpose of the experiment.

Pyrophyllite ($\text{Al}_4\text{Si}_8\text{O}_{20}(\text{OH})_4$) was most widely used as the pressure medium for MAAs until the mid-1970s. At temperatures higher than 600 °C, pyrophyllite decomposes successively into

assemblages of stishovite (SiO_2) + an unknown hydrous aluminum silicate and stishovite + $\text{Al}_5\text{Si}_5\text{O}_{17}(\text{OH})$ at pressures above 10 GPa, and finally into stishovite + corundum (Al_2O_3) at pressures higher than 20 GPa accompanying large volume reduction (Suito, 1986). Therefore, a phase boundary between equilibrated at high-pressure and at high-temperature, determined by the quenching method using a pyrophyllite medium, was generally located in the higher pressure range than the actual one because substantial pressure reduction was accompanied by the decompositions. Instead, semi-sintered MgO with porosity around 35% has been adopted along with the revision of MAAs. A special problem of the MgO medium is its high thermal conductivity compared to pyrophyllite, and it is generally difficult to heat the sample to higher than 1000 °C. Therefore, setting a sleeve of low thermal conductivity, such as ZrO_2 and LaCrO_3 , just outside the heater is indispensable for reducing heat loss and generating high temperatures. Sometimes CaO-doped ZrO_2 is used as a pressure medium because no thermal insulator is needed. However, the ZrO_2 medium brings a blow-out more frequently than MgO. In calibration at room temperature, it is better to contain the calibrant with a soft material such as AgCl in the MgO pressure medium.

In MAAs, a part of the pressure medium extrudes into the anvil gap and forms a gasket according to compression. In order to get better massive support and also to prevent the blow-out, however, gaskets are usually set at the top of the anvil gap in advance (pre-gasket). One criterion to select material for pre-gasket is that it be softer or more compressive than the pressure medium. For the MgO pressure medium, pyrophyllite is adopted as pre-gasket material. In the Kawai-cell the initial size of an octahedron of MgO is substantially larger than the octahedral space formed by truncated triangles of the cubic anvils, and the combination of both is marked by a code such as 14/8 which means that an octahedron of a 14 mm edge length is adopted for the anvils of 8 mm truncation. The thickness of the pyrophyllite gasket is determined by the code.

There is a definite tradeoff when selecting the material and size of the gasket between higher efficiency of pressure generation and higher risk of the blow-out. Yoneda et al. (1984) systematically analyzed the stress states of the gasket and the anvil, and proposed a numerical method to select the best configuration of pre-gasket for effective and safe pressure generation. However, the best choice has been determined empirically considering differences in the mechanical property between the anvil material and the pressure medium, and this is the most difficult but interesting issue of the experiment using the MAA. Actually, each laboratory (or even each researcher) has developed its own assembly and gasket (e.g., Walker et al., 1990). In the case of SD anvil experiments, the baked pyrophyllite gasket, heated at 800–900 °C for a few minutes in air, works well for confining high pressure (Ito et al., 2005). Under these conditions, pyrophyllite dehydrates and forms a sintered assemblage of silimanite (Al_2SiO_5) and an aluminous silicate phase $\text{Al}_2\text{Si}_4\text{O}_{10}$, and the assemblage becomes harder with increased heating time.

2.10.2.4 Fixed Points for Pressure Calibration

Determination of pressure value is of essential importance in applying the experimental results to the Earth's interior,

because pressure inside the Earth as a function of depth is believed to be the most trustworthy parameter. Pressure calibration of the MAA has been carried out by detecting pressure-induced phase transitions in specified materials against applied load or pressure (see [Figure 13](#)). The pressure values of onset of the transformations, the fixed points, were first empirically determined (e.g., [Bundy, 1962](#)) and have been revised by international agreement owing to the development of high pressure technology and research (e.g., [Bean et al. 1986](#)). Recently the in situ x-ray observations in both the MAA and the DAC has expanded their versatility over wider pressure and temperature ranges by using SR. Pressure values determined from the measured volume of the pressure standard material via the equation of state are believed to be the most reliable, because the physical basis for the procedure is clear (see [Section 2.10.4](#)). Nevertheless, pressure fixed points preserve the necessity for an individual laboratory to build up its own calibration and for different laboratories to exchange information in a more orderly manner.

A set of pressure fixed points (PIPS-97), which contained pressure calibration phase transitions at room temperature, equations for well characterized phase transitions at high-pressures, and transitions at high-temperatures, was proposed as the consensus at the time of the First International Pressure Calibration Workshop (IPCW) held at Misasa, Japan, in 1997 ([Ito and Presnall, 1998](#)). The PIPS-97 had to be published

soon under the authorship of all those who wished to participate. As the opportunity for publication has been missed for many years, however, on behalf of the IPCW, the author presents the PIPS-97 with several additional data in [Table 1](#). The PIPS-97 should be improved in accuracy and be expanded to cover wider pressure and temperature conditions in the future.

[Figure 14](#) shows the arrangements of electrodes and calibrant in an octahedral pressure medium for calibration at 300 K. [Figure 14\(a\)](#) is for a metallic calibrant such as Sn and Zr, in which the electric resistance is measured by the four probe method. [Figure 14\(b\)](#) is for detecting semiconductor-metal transition displayed by ZnS and GaP and so on. All the electrodes are taken out to the first or the second anvil surfaces. It is noted that, as the transition kinetics are generally low, the load should be raised slowly around the transition point to detect it accurately.

2.10.3 High-Pressure and High-Temperature Synthesis Experiments

2.10.3.1 Heating Materials

In order to perform synthesis of high-pressure materials and to determine the phase equilibrium relations relevant to elucidation of the Earth's interior, it is necessary to heat the sample to at least 1200 K under prescribed pressure. Sometimes

Table 1 Some phase transitions and characteristic changes in electrical resistance as pressure calibrants (PIPS-97)

<i>P</i> (GPa)	<i>T</i> (°C)	<i>System</i>	<i>Transition</i>	<i>Method</i>	<i>References</i>
2.55	25	Bi	I–II	Electrical resistance	Bean et al. (1986)
3.68	25	Ti	II–III	Electrical resistance	Bean et al. (1986)
5.5	25	Ba	I–II	Electrical resistance	Bean et al. (1986)
7.7	25	Bi	III–V	Electrical resistance	Bean et al. (1986)
9.4	25	Sn	I–II	Electrical resistance	Bean et al. (1986)
12.3	25	Ba	(Upper)	Electrical resistance	Bean et al. (1986)
13.4	25	Pb	I–II	Electrical resistance	Bean et al. (1986)
14.9 ^a	25	CoO	Minimum	Electrical resistance/in situ x-ray	Ito et al. (2012) unpublished data
15.6	25	ZnS	Semi/metal	Electrical resistance	Block (1978)
18.3	25	GaAs	Semi/metal	Electrical resistance	Suzuki et al. (1981)
22	25	GaP	Semi/metal	Electrical resistance	Piermarini and Block (1975)
33	25	Zr	α–β	Electrical resistance	Akahama et al. (1992)
33.2 ± 0.2 ^a	25	Zr	α–β	Electrical resistance/in situ x-ray	Tange (2005)
49 ^a	25	CoO	Maximum	Electrical resistance/in situ x-ray	Ito et al. (2012) unpublished data
60 ^a	25	Fe ₂ O ₃	Inflection to plateau	Electrical resistance	Ito et al. (2009)
3.2	1200	SiO ₂	Qz/Coe	Quench/reversed	Bose and Ganguly (1995)
4.8 → 5.8	800 → 1200	Fe ₂ SiO ₄	α/ <i>r</i>	In situ x-ray	Yagi et al. (1987)
6.2 → 5.9	900 → 1200	CaGeO ₃	Gt/Pv	In situ x-ray	Suzuki et al. (1985)
8.7 → 10.1	1000 → 1530	SiO ₂	Coe/St	In situ x-ray/reversed	Zhang et al. (1996)
12.2 → 14.3	1000 → 1400	Mg ₂ SiO ₄	α/β	In situ x-ray	Morishima et al. (1994)
14.2 → 15.5	1300 → 1600	Mg ₂ SiO ₄	α/β	In situ x-ray	Katsura et al. (2004a,b)
15.1 → 16.0	500 → 750	FeTiO ₃	Il/Pv	In situ x-ray	Ming et al. (2005)
16	1600	MgAl ₂ O ₄	Sp/Per + Cor	Quench/reversed	Akaogi (this meeting)
16.5	1400	MgSiO ₃	CEn/β + St	Quench	Gasparik (1989)
16.5	2150	MgSiO ₃	CEn/Maj	Quench	Presnall and Gasparik (1990)
15.7 → 17.4	800 → 1000	Mg ₂ SiO ₄	β/ <i>r</i>	In situ x-ray/reversed	Suzuki et al. (2000)
19 → 20.8	1200 → 1600	Mg ₂ SiO ₄	β/ <i>r</i>	Quench	Katsura and Ito (1989)
24.8 → 23.1	1000 → 1600	<i>r</i> /Pv + Per		Quench	Ito and Takahashi (1989)

Semi, semiconductor; Qz, quartz; Coe, coesite; St, stishovite; α, olivine; β, modified spinel; *r*, spinel; Gt, garnet; Il, ilmenite; Pv, perovskite; Sp, spinel; Per, periclase; Cor, corundum; CEn, clinoenstatite

^aAdded by the author.

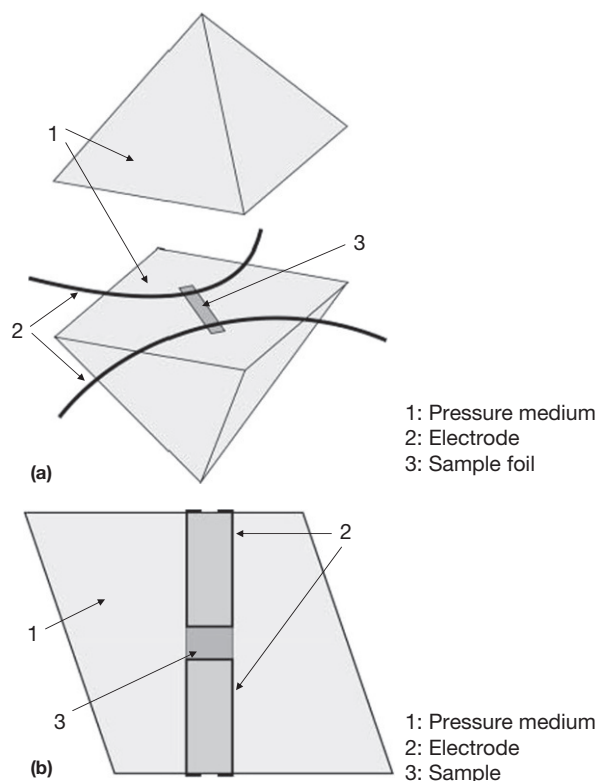


Figure 14 Sample arrangements of octahedral pressure medium for pressure calibration based on the fixed points: (a) a metallic calibrant and (b) semiconductor calibrant (see text).

temperatures up to ~ 3000 K are needed, for example, in melting experiments on mantle materials under lower mantle conditions (Ito et al., 2004). In MAAs, heating the sample is usually carried out by the internal heating method in which a small heater and electrodes are set in the pressure medium and the electric power is supplied to the heater via the anvils. The sample is loaded inside a cylindrical heater or next to a plate heater.

Widely used heating materials are graphite, LaCrO_3 , a composite of TiC + diamond and metals with high melting points such as Pt, Ta, and Re. With these materials, graphite heaters work well to higher than 2500 K at pressures up to ~ 11 GPa, but, at higher pressures, partial transformation of graphite into diamond eliminates this material as a heater. Maximum attainable temperatures using various heating materials depend on shape, size, and configuration of the thermal insulator in the sample assembly, and those temperatures are approximately 1900, 2000, 2700, and 2900 K for Pt, Ta, Re, and LaCrO_3 , respectively. In the cases of metal heaters, dissolution of a small amount of hydrogen from residual water in the sample assembly into the metal greatly lowers melting temperature of the metal. The low attainable temperature of a Ta heater compared to its high melting point would be due to this effect. It is noted that graphite is a typical reducing agent whereas LaCrO_3 is a strong oxidizing agent, especially at a high temperature. It should also be noted that direct contact of LaCrO_3 with silicates causes results in a reaction. Metal and graphite heaters, on the other hand, can serve as sample containers. For the MgO

pressure medium, setting a thermal insulator composed of lower thermal conductivity such as LaCrO_3 or ZrO_2 outside the heater is essential to generating high temperatures, especially in the metal heater.

A compact composite of $\text{BN} + \text{TiB}_2 + \text{AlN}$, called the TiB_2 heater, is commercially available. The TiB_2 heater is chemically stable at high temperatures, and temperatures up to 1800 K can be generated under pressures of several 10s of GPa. Due to its low absorbance for x-ray over a wide range of energy, the TiB_2 heater has been frequently used in in situ x-ray observation experiments using synchrotron radiation (see Section 2.10.4).

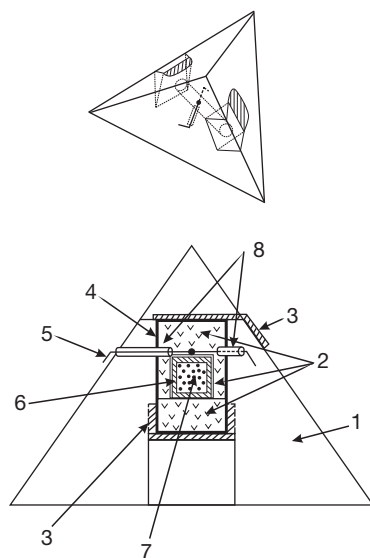
The most remarkable innovation in this realm was the development of the B-doped diamond heater by Shatskiy et al. (2009) which makes it possible to generate temperatures to 3800 K at pressures higher than 20 GPa. They first made a machinable composite of high-purity graphite and a small amount of amorphous boron by cold-pressing. A cylindrically shaped composite was put into the octahedral pressure medium together with a sample inside and a ZrO_2 thermal insulator outside. After pressurizing to 20 GPa, the temperature was raised gradually by supplying electric power. At around 1800 K, the temperature suddenly went down by several hundred degrees within a few minutes at constant voltage. This was accompanied by a noticeable increase in resistance due to the transformation to diamond. After repeated heating and cooling, the temperature rose steadily with a decreasing resistance up to 3800 K. Shatskiy et al. (2009) suggested that doping of 3–5 atomic % Boron works well. They also demonstrated that the B-doped diamond heater is most suitable for the in situ x-ray observation.

Usually experimental temperature is monitored by the *emf* of the thermocouple and controlled by setting an applied voltage to the heater. In the cases of semiconducting heaters such as LaCrO_3 and B-doped diamond, sometimes the temperature increases in a runaway manner due to an abrupt decrease in electrical resistance. This can be avoided by adopting the power (wattage) control system.

2.10.3.2 Heating Assemblies and Temperature Measurement

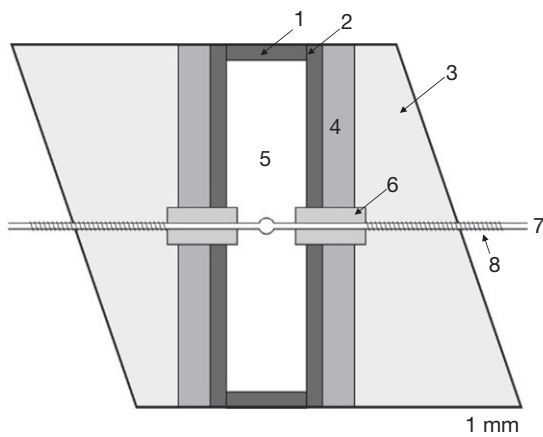
An internal heating system in the MAA was first designed for the tetrahedral press (Bundy, 1962), which is shown in Figure 15. A cylindrical graphite heater is put on the line connecting the midpoints of two opposite edges of the tetrahedral pyrophyllite, and the electric power to the heater is supplied via the anvils and metal strips which lie across notches in the edges of the tetrahedron. The sample, encapsulated within appropriate material, is put into the heater with a spacer. A thermocouple to measure the temperature passes through the cylindrical heater, and the junction is in contact with the capsule. Terminals of the thermocouple wires are in contact with the top surfaces of the remaining anvils or taken out through the gasket to the outside of the apparatus. Such configuration of the parts can be recognized as the archetype of the heating assembly in the MAAs and has been modified for the cubic and octahedral apparatuses.

A basic assembly for an octahedral pressure medium is schematically illustrated in Figure 16. A set comprised of a cylindrical heater and a thermal insulator is placed along the central line between the opposite triangles of an MgO



- 1 Pyrophyllite, 2 BN, 3 Metal electrode
4 Graphite heater, 5 Thermocouple wire
6 Sample container, 7 Sample, 8 Insulating tube

Figure 15 Heating assembly for the Hall's tetrahedral apparatus (see text).



- 1: Lid, 2: Heater, 3: Pressure medium,
4: Thermal insulator, 5: Sample,
6: Electric insulator, 7: Thermocouple,
8: Coil

Figure 16 Cross section of a basic heating assembly for an octahedral pressure medium (see text).

octahedron. Lids at the top and bottom of the heater keep the heater in good contact with the anvil as an electrode. A thermocouple penetrates the pressure medium, thermal insulator, and heater at the midpoint level, which is electrically insulated from the heater by small tubes made of Al_2O_3 or MgO . Outside the sleeves, the wires are passed through thin coils made of the same kind of wires to protect them from break due to flow of pressure medium and gasket. The coils are effective for ductile thermocouples such as Pt/Rh alloys. This assembly is useful in material synthesis and in determination of the subsolidus phase equilibrium by putting the sample

directly into the graphite or metal heater. The heater in a straight cylinder produces a rather steep temperature gradient in the sample along both the longitudinal and radial directions. In a phase equilibrium study, therefore, it is important to adopt the results analyzed only on the portion adjacent to the thermocouple junction in the quenched sample (e.g., Ito and Takahashi, 1989).

Because the outer diameter of the electric insulating sleeve is at least 0.6 mm, two holes made at the center of the cylindrical heater for the sleeves increases the resistance near the center, and the resultant local heating breaks the heater, especially in the case of a small metal heater. This difficulty can be avoided by packing sample powder into the space between the thermocouple and the small hole on the heater instead of inserting the sleeves, but this method does not always guarantee the insulation at high-pressures (Ito and Takahashi, 1989). Moreover, the basic assembly cannot be used in the melting experiment. This problem was solved by moving the holes to the portion close to the cold end of the heater and inserting the thermocouple axially to the sample as shown in Figure 17 (Gasparik, 1989). The thermocouple wires are in contact with the sample holder of metal (Re) to get the junction. The wires cross the Mo ring, and exit the assembly near the apex of a triangular face. The wires are insulated from the heater, the Mo ring, and the WC anvil with alumina ceramic tubes placed in gutters carved out of one of the triangular surfaces of the octahedron.

Temperature in a small cylindrical heater is strongly inhomogeneous in both the axial and radial directions. Kawashima and Yagi (1988) calculated the temperature distribution within a cylindrical heater set in a cubic pressure medium with an edge length of 8 mm using the difference method. Based on the results, they (Kawashima et al., 1990) invented a multi-stepped graphite heater in which the temperature was almost uniform over a 2 mm length in the axial direction. Assessment and improvement of the temperature distribution through the sample were first carried out by Takahashi et al. (1982) for the octahedral assembly based on the solubility of enstatite in the diopside pyroxene coexisting with the enstatitic pyroxene (Lindsley and Dixon, 1976). Using an assembly similar in size to that of Figure 14, they demonstrated that the temperature gradient in a graphite heater tapered by 5° was reduced to one third of that in the straight heater at 1500°C . Recently, van Westrenen et al. (2003) used the kinetics in MgAl_2O_4 spinel growth at the interface between MgO and Al_2O_3 to assess temperature gradients in cylindrical heaters in 18/11 and 8/3 assemblies. They linked the measured thickness to temperature via an appropriate kinetic equation and showed the lengths of the central uniform temperature region for both assemblies. It is remarked that, in the small metal heater adopted for experiments at pressures higher than 25 GPa, a steep temperature gradient of $1\text{--}2\text{ K}\mu\text{m}^{-1}$ was estimated (Ito and Takahashi, 1989; Ito et al., 2004). A temperature gradient in the LaCrO_3 heater is much more moderate compared to the metal and graphite heaters because LaCrO_3 is a semiconductor and the electric resistance of the hot region decreases to lower the temperature there.

Sample temperature is measured by a thermocouple with a junction that is located in or very close to the sample (see Figures 16 and 17). If the junction were not in the sample,

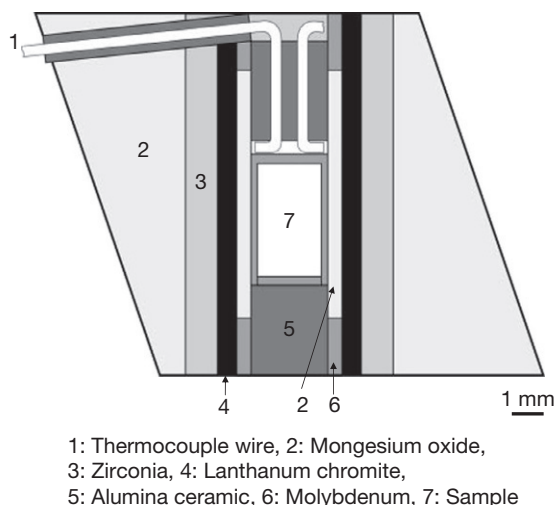


Figure 17 Cross section of a heating assembly. The thermocouple is inserted axially to the rhenium sample capsule (see text). Adapted from Gasparik T (1989) Transformation of enstatite–diopside–jadeite pyroxenes to garnet. *Contributions to Mineralogy and Petrology* 102: 389–405.

the temperature distribution in the heater mentioned earlier should properly be assessed. A formidable experimental problem is that the pressure effects on the emfs of thermocouples are poorly known. Hanneman and Strong (1965) measured the effect for several thermocouples to 1300 °C and 5 GPa and showed that the absolute temperature correction is proportional to the pressure. They indicated the corrections of +40 °C for Pt/Pt10% and +10 °C for chromel–alumel at 5 GPa and 1000 °C, respectively. Later, however, these values were substantially reduced by Getting and Kennedy (1970). As to the W/W-Re thermocouple which has recently been most frequently used in the multi-anvil cell, Li et al. (2003) reported that a reading of the W5%Re/W26%Re varied up to 35 °C compared with that the Pt/Pt10% at 15 GPa and at temperatures up to 1800 °C. The thermocouple wires are taken out of the apparatus and connected to the reference junction kept at 0 °C. Sometimes, however, the wires are conveniently attached to the top of the second-stage anvil. In this case, the temperature there is the reference of the emf, which should have been measured independently for the correction. The anvil-top temperature depends on the output of the heater, the size of the first-stage anvil, and its thermal insulation, etc., but it quickly reaches equilibrium and typically does not exceed 100 °C at the sample temperature of 1500 °C.

The highest temperature that can be measured with a W/WRe thermocouple with reliable accuracy is 2300 °C. Higher temperatures are estimated by extrapolating a relationship between temperature and applied power obtained at lower temperatures.

2.10.3.3 Quench Experiments

It is fortunate that most of the high-pressure phases concerned with the Earth's interior can be recovered to the ambient conditions as metastable phases like diamond. The starting material is first pressurized to prescribed pressure and then heated to the

desired temperature by supplying electric power to the heater for a certain duration. Then temperature quenching of the sample is performed by shutting off the electric supply. The sample temperature generally goes down to a temperature lower than 100 °C from higher than 2000 °C within a few seconds because of the small heater. After a slow decompression, the sample is taken out of the apparatus. The first order transformation accompanying reconstruction of the atomic arrangement is kinetically prevented within such a short period of cooling, and the phase stabilized at the experimental conditions is preserved at high a pressure and room temperature. We can obtain plenty of information on the phase, such as the structure, stability, and physicochemical properties by analyzing the recovered sample with various methods at ambient conditions.

Unquenchable high-pressure phases have been discovered with the development of high-pressure x-ray diffraction methods. The most typical example may be perovskite, a type of CaSiO_3 . Liu and Ringwood (1975) first confirmed the presence of cubic a perovskite-type of CaSiO_3 by in situ x-ray diffraction on the sample in DAC at 16 GPa after heating it with a laser to about 1500 °C. They also observed the retrogressive transformation of the perovskite to glass and $\epsilon\text{-CaSiO}_3$ on release of pressure, which was consistent with the results of the previous quench experiments (Ringwood and Major, 1971). The retrogressive transformation on pressure release is known on several high-pressure-type oxides; for example, rocksalt-type ZnO (Inoue, 1975; Ito and Matsui, 1974), the fluorite-related types of TiO_2 (Liu, 1978), and SnO_2 (Haines and Leger, 1997). The low-pressure phases converted from these compounds after quenching show characteristically broad x-ray diffraction peaks (Ito and Matsui, 1974, 1979). Similarly, recently found post-perovskite phases of MgSiO_3 (Murakami et al., 2004; Oganov and Ono, 2004), MgGeO_3 (Hirose et al., 2005), and MnGeO_3 (Tateno et al., 2006) with the CaIrO_3 structure are all unquenchable. The high pressure phases formed via the second order transformation such as CaCl_2 -types of SiO_2 (Tsuchida and Yagi, 1989), GeO_2 and PbO_2 , and SnO_2 (Haines and Leger, 1997) are also unquenchable.

Any information on unquenchable high-pressure phases can be obtained only by means of in situ measurement, and the in situ x-ray observation at high-pressure and high-temperature is the most important methodology in modern high-pressure Earth science.

2.10.3.4 Crystal Growth at High-Pressure and High-Temperature

Growth of a single crystal at the high-pressure phase is indispensable to determine its crystal structure. In addition, a single crystal with enough size makes it possible to carry out many kinds of measurements, for example, transport properties such as atomic diffusion, thermal conductivity and electrical conductivity, creep experiments, elastic resonance spectroscopy, Raman and Brillouin scatterings, and, more recently, x-ray inelastic spectroscopy, etc. Information collected by these measurements provides important clues to understand the constitution and dynamics of the Earth's interior. Therefore crystal growth has been a major role of the MAAs.

According to the classical homogeneous nucleation theory (Turnbull, 1956) a frequency for occurrence of nucleus embryos

of a new phase in the mother phase is controlled by the free energy difference ΔG between the new phase and the mother phase at the nucleation site and temperature: for example, both the smaller ΔG and the lower temperature are responsible to the smaller frequency. Growth of crystal, on the other hand, is enhanced by high temperature. Therefore favorable conditions for growth of large single crystals would be at relatively high temperature but should be very close to the phase boundary, which means a small excess pressure over the phase boundary for the growth of the high-pressure phase. This view was supported through the systematic experiments on the growth of γ - Ni_2SiO_4 spinel in olivine crystals by Hamaya and Akimoto (1982). Sawamoto (1986) succeeded in growing crystals in both the β - and γ -phases of compositions $(\text{Mg,Fe})_2\text{SiO}_4$ with sizes larger than 200 μm at temperatures of 1700–2200 °C and pressures within $\pm 5\%$ of the γ - β phase boundary. Pressure and temperature conditions, at which MgSiO_3 garnet (Angel et al., 1989) and ilmenite (Horiuchi et al., 1982) single crystals were synthesized, were also around the phase boundary between both phases.

For high-pressure phases that are difficult to grow, appropriate flux could enhance the crystal growth at relatively low temperatures. Sinclair and Ringwood (1987) synthesized stishovite crystals in size to 230 μm by keeping silicic acid with 40% of water at 9 GPa and 700 °C for 45 min. Endo et al. (1986) obtained stishovite crystals elongated to several hundreds of micrometers at 12 GPa and 1300 °C by using Li_2WO_4 as flux. Ito and Weidner (1986) grew MgSiO_3 perovskite crystals with sizes to 200 μm by cooling the MgSiO_3 melt saturated with H_2O from 1830 °C slowly at 27 GPa. Recently single crystals of perovskites with MgSiO_3 , and $(\text{Mg,Fe,Al})(\text{Si,Al})\text{O}_3$ compositions larger than 300 μm have been synthesized in NaCl melt by cycling the temperature in a sample chamber (Dobson and Jacobsen, 2004). More recently, Anton et al. (2007) succeeded in growing MgSiO_3 perovskite crystals with a size exceeding 1 mm by adopting water as flux in a sophisticated sample capsule. Potential materials as flux for the crystal growth under the high-pressure and high-temperature conditions may be water and some sorts of borates, carbonates, alkali halides, etc.

It is no wonder that a crystal bigger than the sample capsule cannot be grown. Therefore big multi-anvil presses recently installed (e.g., Frost et al., 2004) must be very advantageous to crystal growth because these presses can compress a larger octahedron of pressure at medium to higher pressures.

2.10.3.5 Electrical Conductivity Measurement

Electrical conductivity within the mantle is explored by examining the electrical current induced by change in the external magnetic field (MT probing) and by analyzing the transient and secular variations of the magnetic field originating from the core (GDS probing). Although proposed distributions of electrical conductivity versus depth in the mantle are model dependent, the following characteristic can be noted on the conductivity-depth profile: conductivity increases in the mantle from 10^{-4} to 10^{-2} S m^{-1} at the top to $\sim 10^5 \text{ S m}^{-1}$ at around 800 km depth (e.g., Utada et al., 2003) in a manner reflecting variation of the tectonic setting (e.g., Neal et al., 2000). In the lower mantle, the conductivity is almost constant to 2000 km depth, with $3\text{--}10 \text{ S m}^{-1}$ with less lateral heterogeneity compared to the upper mantle.

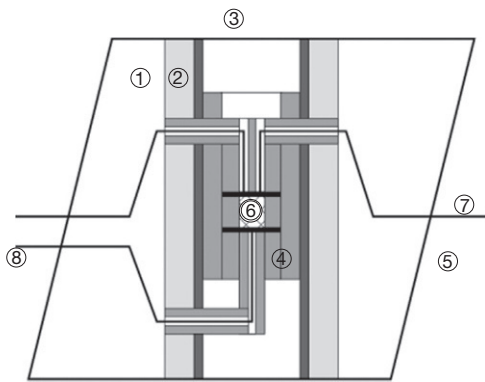
Almost all mantle minerals are regarded as ionic insulators with large energy gaps, for instance, 6.4 eV (forsterite) and 8 eV (quartz). The mechanism of creating an electrical current is through thermally activated diffusion of the whole ion through the crystal (ionic conduction) or thermally activated charge transfer between neighboring ions of different valence (hopping conduction). So, temperature is the most dominant quantity to control the electrical conductivity. At high pressure, on the other hand, the latter mechanism would become dominant, and the conductivity increases with increasing pressure because the jump distance between sites decreases. The conductivity of the mineral also strongly depends on chemical composition, especially iron content and the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio (and thus on oxygen fugacity). The introduction of a small amount of water into nominally anhydrous minerals substantially increases the conductivities due to the migration of the proton (e.g., Yoshino et al., 2006).

By measuring the electrical conductivity of mantle minerals over wide pressure and temperature conditions, one can evaluate their activity energy ΔE and activation volume ΔV for conduction depending on the conduction mechanism. These quantities make it possible to extrapolate the measured conductivity to the conditions corresponding to the deep mantle. Comparison of the estimated conductivities with the observed profile leads to an inferred temperature profile if the mineralogy and chemistry there is constrained.

Electrical conductivity at high pressure and temperature has been measured using both the DAC and the Kawai-type apparatus. It is remarkable that conductivity measurement was carried out on silicate perovskite and post-perovskite in the laser heated DAC up to 143 GPa and 2500 K by Ohta et al. (2008). Method of electrical conductivity measurement in the Kawai apparatus was also developed, in which measurement is carried out up to 25 GPa and at well-defined temperatures to 1700 °C under the controlled oxygen fugacity (Katsura et al., 1998). And accessible pressure has been extended to 35 GPa by adopting SD anvils (see Section 2.10.4.7) (Katsura et al., 2007). The thermal state (Katsura et al. 1998) and the textural structure (Yoshino et al., 2008) of the lower mantle were discussed based on electrical conductivities of silicate perovskite and ferropericlase.

A cross section of the assembly for measuring electrical conductivity in the Kawai apparatus is schematically shown in Figure 18 (cf. Katsura et al., 1998). The assembly is for the 8.0/3.0 combination (see Section 2.10.2.3). The pressure medium is composed of primary MgO. A cylindrical heater is put in a thermal insulator sleeve. The sample is embedded in an Al_2O_3 container which is put between thin Fe disks. The Fe disks are used to keep the oxidation state of the sample below the Fe-FeO buffer, and also to work as electrodes for the electrical conductivity measurement. The thermocouple is mechanically connected to one Fe disk to measure the sample temperature and also to serve as electrodes for electrical conductivity measurement. The thermocouple is insulated from the heater by Al_2O_3 sleeves. The other Fe disk is connected to a metallic lead for an electrode of electrical conductivity measurement.

The electrical conductivity is measured according to the electric circuit shown in Figure 19. The sample is connected to a reference resistance, variable in a range 50–1 M Ω , in a series. A sinusoidal alternating voltage (0.01–0.1 Hz and



① MgO + 5%Cr₂O₃ ② Thermal insulator ③ Heater ④ Al₂O₃ or MgO
⑤ Fe plate ⑥ Sample ⑦ Thermocouple ⑧ Electrode

Figure 18 A schematic drawing of the sample assembly of 8/3 cell for electrical conductivity measurement.

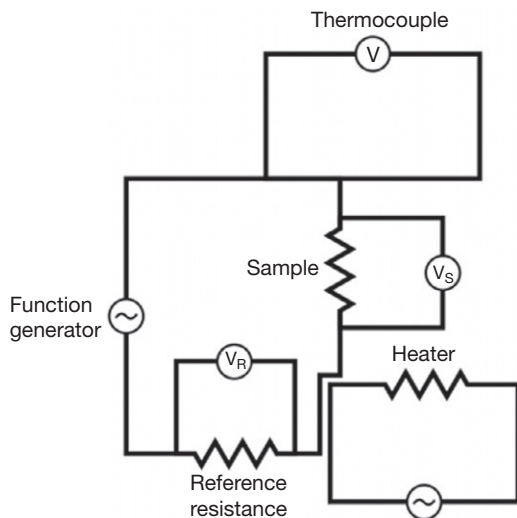


Figure 19 Circuit for electrical conductivity measurement.

0.1–10 V_{peak-to-peak}) is applied to this circuit by a function generator. The voltages applied on the sample (V_S) and reference resistance (V_R) are monitored by two digital millimeters. The sinusoidal signal from the function generator is applied to the sample through one side of the thermocouple and the lower guide block. The voltage applied to the sample is measured using the other side of the thermocouple and the lower guide.

The obtained data points are fitted to the function $V(t) = a + bt + A \sin[\omega(t - \alpha)]$, where t is time and others are fitting parameters, in order to obtain the complex voltages applied on the sample and reference (V_S) and (V_R). The impedance of the sample (Z_S) is obtained from the reference resistance (R_R) and the ratio of the voltages of the sample and reference, namely,

$$Z_S = R_R(V_S/V_R) \quad [2]$$

Assuming that the impedance of the sample is composed of the resistance of the sample (R_S) and one capacitance in

parallel with the sample, the resistance of the sample is obtained from the following equation:

$$1/Z_S = i/R_S + j\omega C \quad [3]$$

After decompression and recovery of the assembly, a cross section of the assembly is made along the heater axis, and the thickness and diameter of the sample is measured. The electrical conductivity of the sample is calculated from the resistance and the dimensions of the sample.

Methodology of electrical conductivity measurement of mantle minerals at high P–T conditions are comprehensively reviewed by Yoshino (2010).

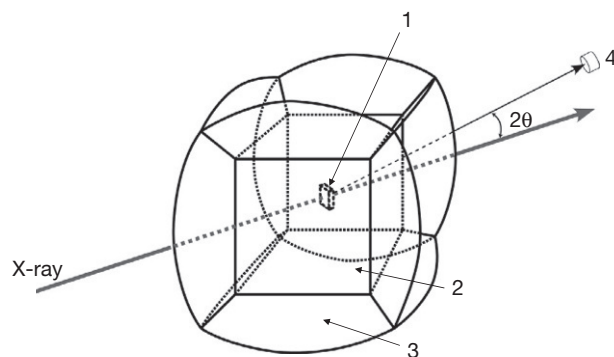
2.10.4 In Situ x-Ray Observations Using SR

2.10.4.1 Methods of in Situ x-Ray Diffraction Using MAAs

It is desirable to directly observe the sample under the high-pressure and high-temperature conditions. The desire was met in the DAC via the in situ optical observation and the x-ray diffraction because diamond was highly transparent for electromagnetic waves of a broad range of frequency. An x-ray diffraction study in the tetrahedral anvil apparatus, on the other hand, was also developed by Hall et al. (1964). The MoK α radiation collimated to $\sim 500 \mu\text{m}$ was introduced into the tetrahedral pressure medium composed of composites LiF, B and plastic through the anvil gap, which then was irradiated to the sample packed in NaCl at the center of tetrahedral pressure medium. The diffracted x-ray was taken out from the opposite anvil gap over the diffraction angles of $\sim \pm 50^\circ$. The diffraction peaks of both the sample and NaCl were recorded on a film or by a counter. The state of the sample such as volume and structure are continuously monitored as a function of pressure which was derived from the volume of NaCl via the EOS for NaCl proposed by Decker (1965). Hall et al. (1964) observed in situ structural transitions of Cs and the change in electrical resistance to 8 GPa simultaneously.

Inoue and Asada (1973) attached an x-ray diffraction system to the DIA-type apparatus with a pressure medium of a composite of boron and epoxy. They carried out in situ high-pressure and high-temperature x-ray diffraction study up to 13 GPa and 1000 °C by setting a paired graphite heater in the pressure medium. Later Inoue (1975) successfully interfaced the energy dispersive system with the DIA apparatus as schematically shown in Figure 20. He used the polychromatic x-ray from the W target and the solid state detector (SSD) for counting the diffracted x-ray. Employing the revised Decker's (1971) NaCl pressure scale, Inoue revealed a shocking fact that the pressure values in the quench experiment had been overestimated: that is, the sample pressure fell substantially by heating of 7.5 GPa at room temperature to 5 GPa at 1400 °C under the fixed press load. Moreover, Inoue demonstrated that the phase boundary for the wurtzite–rocksalt transition in ZnO determined by means of in situ x-ray diffraction was dramatically different from that determined by quench method (Bates et al., 1962).

The energy dispersive method has marked advantages over the angle dispersive method in the x-ray diffraction study using the MAAs. Firstly, information on a wide range of d-spacing is collected at once from the intensity/energy profile of the



1: Sample, 2: Cubic pressure medium, 3: Gasket, 4: Counter

Figure 20 x-Ray diffraction geometry in the energy dispersive method by using the DIA type apparatus. Polychromatic x-ray is introduced to the sample through the gasket and pressure medium of boron and epoxy composite. The diffracted x-ray is counted by the SSD set at angle 2θ from the direction of the incident x-ray. Adapted from Figure 2 of part in Inoue K (1975) *Development of High Temperature and High Pressure x-Ray Diffraction Apparatus with Energy Dispersive Technique and Its Geophysical Applications*. PhD Thesis, The University of Tokyo.

diffracted x-ray collected at the fixed diffraction angle 2θ by SSD. Secondly, by using high-energy x-ray (usually 20 to ~ 120 keV), absorption through the pressure medium and gasket is much reduced compared to usage of the characteristic x-ray such as $\text{MoK}\alpha$ radiation. And thirdly, the diffraction area and location in the sample is unmoved for the fixed diffraction angle. This is specifically important for the high temperature x-ray diffraction study using the MAA because the sample in a small heater is usually under a steep temperature gradient as mentioned already.

2.10.4.2 Multi-anvil System Interfaced with SR

The technical development in the in situ x-ray observation recently expanded the versatility of the MAAs. Inoue's (1975) work pointed out that the phase boundaries determined by quench method might contain considerable uncertainty and should be checked by the high P-T in situ observation. Initially the rotated anode x-ray source was exclusively employed with the DIA type apparatus in experiments for both determination of phase boundaries (e.g., Yagi and Akimoto, 1976) and acquisition of compression data on geophysically important minerals (e.g., Sato, 1977). In these works, it took a rather long time to collect reliable diffraction patterns because the x-ray source was not sufficiently strong.

In the early 1980s, however, SR x-ray sources became available for high-pressure experiment by the MAAs at the Photon Factory (PF), National Laboratory for High Energy Physics, Japan. A new DIA-type apparatus named MAX 80 (Shimomura et al., 1985) was installed at the Photon Factory (PF), National Laboratory for High Energy Physics, Japan. The SR x-ray has high flux, high localizability, low beam divergence, and high flux distribution in a hard x-ray range. These characteristics are quite appropriate to obtain a clear diffraction pattern of the sample under compression within a short period. The high brilliant beam made it especially possible to study reaction

kinetics of high-pressure transformation in silicate (e.g., Rubie et al., 1990) and to measure the viscosity and density of silicate melt by means of x-ray radiography.

The great success of MAX 80 promoted the installations of the DIA type apparatus (SAM 85) interfaced with the SR facility at the National Light Source, Brookhaven National Laboratory, USA (Weidner et al., 1992). The second DIA apparatus (MAX 90) at PF was equipped with sintered diamond anvils with a top square edge of 4 mm and the experimental conditions up to 15 GPa and 1500 °C was realized (Shimomura et al., 1992). In order to extend in situ x-ray observation to higher pressure, however, the system was transferred into the double-staged system by putting the Kawai-cell into the cubic space of the DIA apparatus (Figure 7). An octahedral sample assembly was adopted instead of the cubic one in the single-staged DIA system. Funamori et al. (1996) employed SD cubes with 10 mm edge length for the Kawai-cell anvils, and determined the thermoelastic properties of MgSiO_3 perovskite up to 30 GPa and 2000 K.

Based on the accomplishments of the double-staged multi-anvil system at PF, a combination of the DIA press and the Kawai-cell (SPEED-1500) was constructed on the beam line BL04B1 at SPring-8, a third generation synchrotron radiation facility in Hyogo prefecture in Japan, in 1997 (Utsumi et al., 1998). Recently a sister apparatus SPEED-Mk. II (Katsura et al., 2004a,b) was installed in the same beam line in series with SPEED-1500.

x-Ray optics adopted for both the apparatuses is schematically illustrated in Figure 21. An incident white x-ray beam is introduced to the sample in the octahedral pressure medium through anvil gaps at both the first- (the DIA apparatus) and the second-stage (the Kawai-cell) anvils. Diffracted x-ray was taken out also between the anvil gaps horizontally at the fixed angle of 2θ and collected by the Ge SSD through the collimator and the receiving slits, which ensure the fixed angle of 2θ . The x-ray that directly passes through the pressure medium and gaskets enters the charge coupled device (CCD) camera to make an x-ray image of the sample, which is a great help to determine the shooting point in the sample assembly. Both SPEED-1500 and SPEED-Mk. II have a compressive force of 15 MN. Advantage of the latter over the former, however, is that the whole apparatus of SPEED-Mk. II can be rotated by $\pm 9^\circ$ around the diffraction center which is achieved by adjusting the apparatus position precisely. This function is quite effective in obtaining the proper diffraction profile for the sample of progressed grain-growth or that with the preferred orientation of crystal axes.

2.10.4.3 Experimental Procedures for In Situ x-Ray Diffraction Study

In the energy dispersive diffraction method the diffracted x-ray is collected by SSD and analyzed by a multi-channel analyzer. In the multi-channel analyzers for SPEED-1500 and SPEED-Mk. II, 4096 channels are allotted to the energy range from 8 to 120 keV with an energy width of 0.027 keV per channel. The interplanar spacing d that causes diffraction in crystal is given by:

$$d = ch/2E \sin \theta \quad [4]$$

where c , h , E , and θ are the speed of light, the Planck's constant, the energy of x-ray, and the diffraction angle, respectively. The

multi-channel analyzer is calibrated by detecting the characteristic radiations of several metals such as Cu, Ag, Mo, Ta, Pt, Au, and Pt on the assumption that the energy of each channel is a linear function of the channel number. The 2θ value is calibrated by collecting the diffraction patterns of the standard materials such as Si, Au, and MgO, adopting the d-value of each peak calculated using eqn [1].

Figure 22(a) shows a cross section of our typical sample assembly for in situ x-ray observation to determine the phase equilibria at SPring-8, using SD cubes as the second-stage anvils (Ito et al., 2010a,b). The SD cube with an edge length of 14 mm and a truncated corner of 1.0 mm is employed for this assembly. Octahedron of MgO + 5% Cr₂O₃ with an edge length 4.6 mm is used as the pressure medium. A fine mixture of the sample and pressure marker (typically Au or MgO) is directly put into a cylindrical TiB₂ heater which is set at the center of the octahedron perpendicular to the opposed

triangular surfaces. Sometimes powders of the sample and the pressure standard are put separately at the center of the heater. LaCrO₃ parts are for thermal insulation and the powdered diamond is placed to minimized extrusion of Re electrodes into the anvil gaps to reduce possibility of blow-out.

By adopting the TiB₂ heater we can see through the sample and the thermocouple radiographically by the CCD as shown in Figure 22(b). A polychromatic x-ray beam typically collimated to 100 μ m vertically and 50 μ m horizontally is introduced to the sample to acquire the diffraction profiles. The 2θ is typically 6°, and the length of the diffraction area with a lozenge shape is about 1.3 mm for an x-ray beam of horizontal width of 50 μ m and the collimator with a diameter of 50 μ m. Therefore, in addition to diffraction from the sample and/or the pressure standard, that from TiB₂ is also collected at once. However, the latter is relatively weak and does not interrupt the analysis of the former. The pressure is determined from the

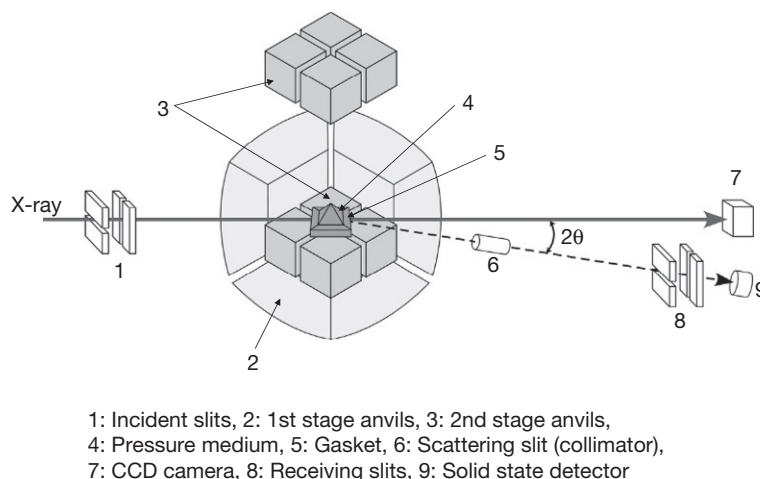
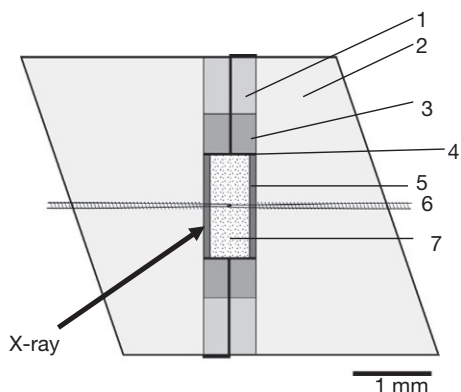
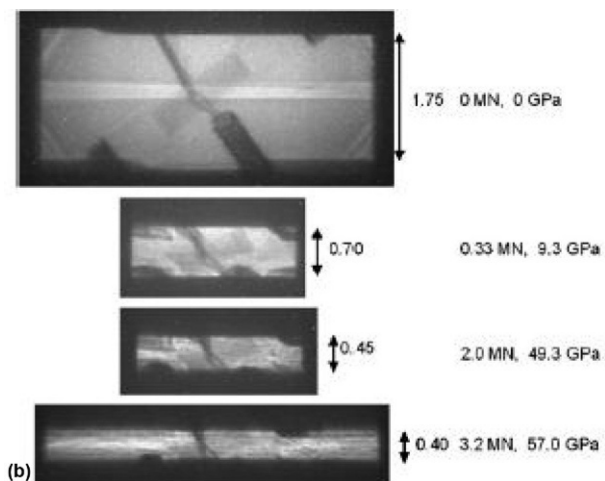


Figure 21 Schematic drawing of the x-ray optics adopted in double-staged system combining the DIA-type guide block and the Kawai-cell (see text).



- 1: Powdered diamond, 2: Pressure medium (MgO + 5%Cr₂O₃)
3: LaCrO₃, 4: Re electrode, 5: TiB₂ heater, 6: Thermocouple
7: Sample (sample + 0.1 Au)

(a)



(b)

Figure 22 (a) Schematic drawing of a cross section of the octahedral sample assembly for the in situ x-ray observations using SD cubic anvil with 1.0 mm truncation. (b) CCD images of the sample and the thermocouple through the TiB₂ heater at various press load (in MN). Unit of numbers for anvil gaps is mm.

measured unit cell volume of the pressure standard material and the experimental temperature using the equation of state (e.g., Tsuchiya, 2003 for Au and Matsui et al., 2000 for MgO).

The LaCrO₃ cylindrical heater with a coaxial ZrO₂ thermal insulator, in which the sample is loaded, is set perpendicular to the x-ray. In this case, parts of the cylindrical LaCrO₃ heater and ZrO₂ insulator are removed and replaced by low atomic number materials such as MgO and diamond to secure the passes of incident and diffracted x-ray (e.g., Ono et al., 2000). The x-ray pass is secured by using two platy heaters, in which configuration the sample and the pressure marker are placed between them (e.g., Irifune et al., 1998).

2.10.4.4 Pressure Determination

One of the primary advantages of the in situ x-ray diffraction experiment is that pressure can be monitored continuously in real-time. As mentioned in Section 2.10.2.4, accuracy of pressure determination is of great importance in experiments concerning the Earth's interior. For example, global topographies of 410 and 660 km seismic discontinuities are mapped with a resolution of 1–5 km (Flanagan and Shearer, 1998). Pressure increases in the mantle by a ratio of 0.04–0.05 GPa km⁻¹. If one tries to assign the discontinuities to the phase transformations, therefore, the phase boundaries should be determined at least within an accuracy of 0.25 GPa.

2.10.4.4.1 Pressure-standard materials and the pressure scales

Pressure determination of the in situ x-ray observation using the MAA is carried out based on the P–V–T EoS of the internal standard material. First the unit cell volume is measured at the prescribed press load and temperature and then it is converted to pressure via the EoS. Therefore the most basic requirement for the pressure-standard material is that its EoS is reliably established over wide pressure and temperature ranges. Additionally requirements for pressure-standard materials, some of which being mutually contradictory, are relatively low absorption for x-rays, simple diffraction profile, low bulk modulus, low-yielding strength, chemical inertness, high melting temperature, no phase transition, low-grain growth rate, etc. under high pressure and temperature. Pressure standards which have been most frequently used in the in situ experiments for high-pressure Earth sciences are NaCl, MgO, Au, and Pt. In MAA experiments, the pressure-standard material is placed nearby the sample or powder-mixed with the sample.

The EoSs of the standard materials are expressed as

$$P(V, T) = P(V, 300\text{ K}) + P_{\text{th}}(V, T) \quad [5]$$

where $P(V, T)$ is the pressure at volume V and temperature T , and the first and second terms in the right-hand side are the pressure at V and 300 K, and the thermal pressure difference between at T and 300 K under constant volume V , respectively. As $P(V, 300\text{ K})$, Birch-Murnaghan EoS (Birch, 1952) or Vinet et al.'s (1987) EoS has frequently adopted. The $P_{\text{th}}(V, T)$ is approximated to $C_V(\gamma/V)(T - 300)$ (C_V , specific heat at constant volume; γ , Grüneisen constant). Necessary parameters to construct the concrete EoSs are selected to reproduce various thermoelastic quantities experimentally established for the material, such as

bulk modulus and thermal expansion and their pressure and temperature derivatives. Shock compression data are very important information to constrain the EoSs. For Au and Pt, electronic thermal pressure is required as an additional term at high temperatures (Tsuchiya and Kawamura, 2002).

If the bulk modulus ($K_T = \rho(\partial P/\partial \rho)_T$) is known as a function of density (ρ), on the other hand, one can obtain a primary EoS by integrating K_T with respect to ρ without reliance on other calibration. The primary EoSs for MgO have been proposed based on the simultaneously measured density by the x-ray diffraction and the elastic wave velocities from Brillouin scattering (Zha et al., 2000) and ultrasonic method (Kono et al., 2010).

Many EoSs have been proposed as the pressure scales, which, however, seem to be gradually selected through the use and mutual comparison. Comparison of pressure values deduced by a different standard has also been carried out. In the following, characteristics of standard materials are briefly described with few arbitrarily chosen EoSs recently adopted. It should be noted that the discrepancy between the EoSs for each material generally increase with pressure and reaches ~5 GPa at 100 GPa. The discrepancies, on the other hand, don't seem to be sensitive to temperature.

NaCl as the pressure standard has been used for 50 years since Hall et al. (1964). Decker (1965, 1971) first constructed the EoS of NaCl as a practical pressure scale, which was later revised by Brown (1999). An advantage of the NaCl scale is high-precision in pressure determination due to the low bulk modulus (25 GPa under ambient conditions); for example, volume determination within 0.1% precision is converted to precision of pressure 0.14 GPa at around 20 GPa. Nevertheless its relatively low melting temperature hinders from usage of NaCl for experiments at high temperatures due to the pronounced anharmonic contributions to the EoS and noticeable grain growth. It should be noted that NaCl transforms from B1 to B2 structures, which occurs at 22–20 GPa and at 1600–2000 K (Nishiyama et al., 2003). The EoS of B2 type of NaCl at room temperature was carefully constructed up to 68 GPa by Sata et al. (2002) based on their compression data and pressure scales of MgO (Speziale et al., 2001) and Pt (Holmes et al., 1989), which was recently followed by Sakai et al. (2011) who extended the EoS to 304 GPa. The NaCl scale has rarely been used in the recent MAA experiments but rather often in the DAC experiments.

Some of the disadvantages of NaCl can be avoided by MgO, which possesses a larger bulk modulus of 164 GPa at ambient conditions, higher melting temperature (3100 K at 0 GPa), a relatively low-grain growth rate, and a no-phase transformation of up to a few hundreds of GPa. The most frequently adopted MgO scales would be Matsui et al. (2000) and Speziale et al. (2001).

As Au and Pt are not active with oxides and silicates, they are frequently mixed with the sample in weight ratios from 1/20 to 1/10. The pressure standard in a composite indicates somewhat erroneous pressure value until the stress homogenization in the composite is achieved by heating. From this viewpoint, a low rigidity of Au (27.6 GPa) is more favorable than Pt (62.2 GPa). The composite is also effective to prevent the grain growth of Au and Pt at high temperature. Au is more often used than Pt because its bulk modulus (166 GPa) is definitely lower than

that of Pt (273 GPa) and thus more sensitive to pressure. However, the higher melting point of Pt (2045 K at 0 GPa) makes it favorable to high-temperature experiments. The most frequently adopted Au scales would be Anderson et al. (1989), Tsuchiya (2003), Matsui (2010), and Dorogokupets and Oganov (2007) and those for Pt would be Holmes et al. (1989) and Dewaele et al. (2004).

2.10.4.5 Application to Phase Equilibrium Studies

Although the pressure scales are not perfect ones at present and contain some uncertainties especially at high temperature, it is certain that the in situ x-ray diffraction method is more reliable than the quench method in determining pressure values of the MAA. Therefore important phase boundaries in high-pressure Earth sciences defined by the quench experiments have thoroughly been reinvestigated by means of in situ x-ray diffraction as summarized in Table 2 (see a review by Katsura (2007) for detail). For the transformations that occur at pressures less than 20 GPa, both the quench and the in situ x-ray methods have offered generally consistent boundaries. Especially extrapolation of the phase boundaries for the α - β and β - γ transformations in Mg_2SiO_4 determined in situ to higher temperature suggests their locations very close to those determined by the quench method as shown in Figure 23. These situations may indicate the carefulness of the quench experiments and the reliability of the NaCl pressure scale.

However surprisingly variable results were reported on the phase boundary for the dissociation of Mg_2SiO_4 (γ) into MgSiO_3 (perovskite) and MgO (periclase) as illustrated in Figure 24. Location of the boundary was the most

controversial issue relevant to interpretation of the 660 km discontinuity. Phase boundaries determined based on the Anderson et al.'s (1989) Au scale are located ~ 2 GPa lower than that determined based on Speziale et al.'s (2001) MgO scale (Fei et al., 2004b), in harmony with discussion by Fei et al. (2004a). However, there are marked difference in slope for the phase boundaries between those by Katsura et al. (2003) and Fei et al. (2004b) and that by Irifune et al. (1998), although pressure determination in all the works were carried out based on the Anderson et al.'s (1998) Au scale. Fei et al.'s (2004b) boundary based on Speziale et al.'s (2001) MgO scale is closely located to that of Ito and Takahashi (1998) determined by quench experiment and supports the conventional interpretation that the 660 km discontinuity would be caused by the dissociation of ringwoodite.

In addition to the mutual inconsistency among different pressure scales, there are at least two issues to make the determination of phase boundary ambiguous: temperature determination and the reaction kinetics of phase change.

As pressure scale is a function of temperature as well as the volume of the standard material, precise temperature determination is of essential importance to define pressure with high accuracy. For example, a temperature variation of 100 K causes that of 0.5 and 0.7 GPa at ~ 1800 K in the MgO and the Au scales, respectively. In the experiments at pressures higher than 20 GPa, the heater in the sample assemblage is generally small (see Figure 22) and a steep temperature gradient is inevitably produced in the assemblage. Therefore temperatures of the sample and the standard differ from that indicated by the thermocouple. It should be also noted that the diffraction area unavoidably covers a region of varying temperature due

Table 2 Phase boundaries, P (GPa) = aT (K) + b , for geophysically important reactions determined by means of in situ x-ray diffraction and the quench experiment in the multi-anvil apparatus

Compound	Reaction ^a	a (GPa K ⁻¹)	b (GPa)	T -range (K)	P -marker ^b	References
SiO_2	Coe/St	0.0012	7.7	770–1370	NaCl(B)	Yagi and Akimoto (1976)
		0.002	6.2	137–1800	NaCl(B)	Zhang et al. (1996)
		0.002	6.8	870–1470	Q	Suito (1977)
Fe_2SiO_4	β/γ	0.0019	2.9	1073–1473	NaCl(B)	Yagi et al. (1987)
		0.0044	0	973–1473	Q	Akimoto et al. (1965)
Mg_2SiO_4	α/β	0.0032	8.9	1013–1673	NaCl(B)	Morishima et al. (1994)
		0.004	7.8	1600–1900	NaCl(B)	Katsura et al. (2004b)
		0.002	11.1	1473–1873	Q	Katsura and Ito (1989)
	β/γ	0.0069	8.4	927–1327	NaCl(B)	Suzuki et al. (2000)
		0.004	13.1	1473–1873	Q	Katsura and Ito (1989)
		0.003	26.7	1673–2073	Au(A)	Irifune et al. (1998)
	$\gamma/\text{Pv}+\text{Pe}$	–0.0004 to –0.0017	22.7–25.5	1500–2000	Au(A)	Katsura et al. (2003)
		–0.0008	23.2	1673–2173	Au(A), Q	Fei et al. (2004b)
		–0.0013	25.5	1673–2173	MgO(S), Q	Fei et al. (2004b)
		–0.0028	28.3	1373–1873	Q	Ito and Takahashi (1989)
MgSiO_3	Il/Pv	–0.0023	26.6	1073–1573	NaCl(B)	Kato et al. (1995)
		–0.0035	27.3	1300–1600	Au(A)	Ono et al. (2001)
		–0.0029	28.4	1300–1600	Au(J)	Ono et al. (2001)
		–0.0027	25.09	1673–2273	Au(A)	Hirose et al. (2001)
		–0.0025	26.8	1273–1873	Q	Ito and Takahashi (1989)

^aCoe, coesite; St, stishovite; α , olivine; β , modified spinel; γ , spinel; Pv, perovskite; Pe, periclase; Il, ilmenite.

^bNaCl(B): Brown's (1999) NaCl scale; Au(A): Anderson et al.'s (1989) Au scale; Au(J): Jamieson et al.'s (1982) Au scale; MgO(S): Spaziale et al.'s (2001) MgO scale; Q: quench experiment.

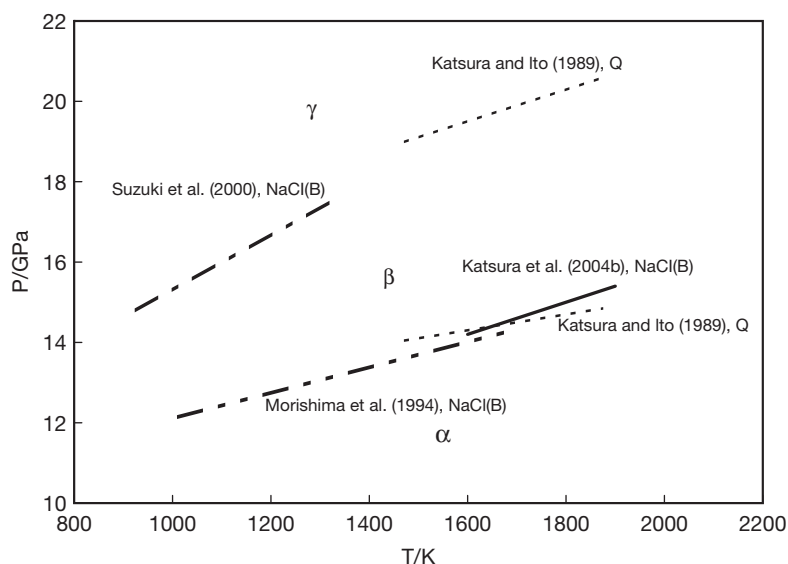


Figure 23 The phase boundaries for the α - β and β - γ transformations in Mg_2SiO_4 determined by in situ x-ray diffraction method (Katsura et al., 2004b; Suzuki et al., 2000) together with those determined by quench method. All the phase boundaries in general consistency.

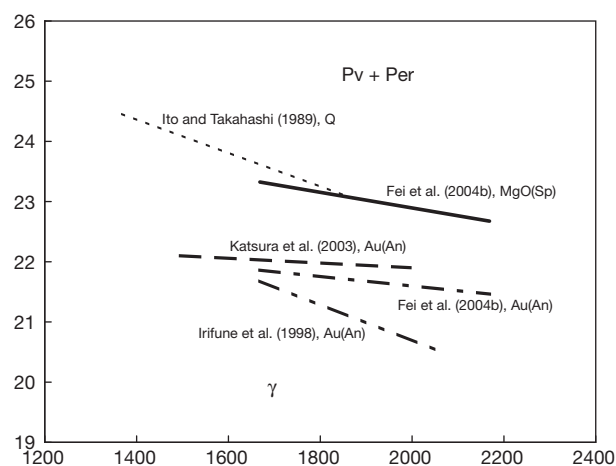


Figure 24 Phase boundaries for the dissociation of Mg_2SiO_4 (γ) into MgSiO_3 (perovskite) and MgO (periclasite) determined by in situ x-ray diffraction method (Fei et al., 2004b; Irifune et al., 1998; Katsura et al., 2004b) together with that determined by quench method (Ito and Takahashi, 1989). Phase boundaries determined based on the Anderson et al.'s (1989) Au scale are located at ~ 2 GPa lower than (Fei et al., 2004b) determined based on Speziale et al.'s (2001) MgO scale.

to the steep temperature gradient through the sample. To minimize this effect the sample length is usually limited to less than 0.5 mm (cf. Figure 22). Another difficult problem is that pressure effect on emf of the thermocouple is not quantitatively known at high P-T conditions (Section 2.10.3.2).

In the course of progress of the in situ x-ray diffraction study, it has become clear that the reaction kinetics play an important role in determining the phase relations. It is frequently observed that the starting material of low-pressure phase rapidly transforms into the intermediate high-pressure phase at relatively low temperature in the course of the first heating (e.g., Irifune et al.,

1998; Katsura et al., 2003; Yagi and Akimoto, 1976) and the new phase is so refractory that substantial excess pressure is required to promote further transformation (Katsura et al., 2003; Ono et al., 2001). These features are interpreted as follows. The finely powdered starting material is further pulverized by compression at room temperature as seen from the associated broadening of the diffraction peaks. The fractured grain boundaries and defects formed inside the grains make the starting material extremely reactive, providing nucleation sites for the new phase. The resultant new phase, on the other hand, is well in crystalline state with sharp diffraction peaks. It is difficult to increase reactivity of the high-pressure phase once formed. This situation hinders observing the reverse reaction which is required to define the precise phase boundary.

2.10.4.6 Viscosity Measurement by x-Ray Radiography

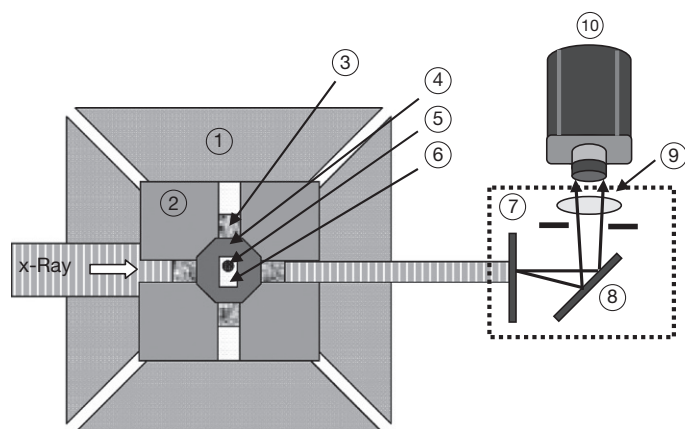
There are two types of liquids in the 'solid Earth,' silicate melt (magma) in the crust and the mantle and molten iron alloy forming the outer core. The viscosity of both the liquids at high pressure is the most crucial property for understanding various magmatic processes and dynamic structure of the outer core. The characteristics of x-rays emitted from SR, high flux and low beam divergence, are appropriate to measure viscosity at high pressure by the in situ falling sphere method in the MAA. Kanzaki et al. (1987) first measured viscosities of $\text{NaAlSi}_3\text{O}_8$ (albite) and $\text{Na}_2\text{O} \cdot \text{SiO}_2$ melts up to 3 GPa using the DIA-type apparatus at PF. The shadow images of the falling sphere of Pt and/or Mo (100–300 μm radius) in the melt were clearly observed on the TV, and the viscosity was derived from the falling velocity via Stokes' law.

Now the in situ falling sphere viscometry is mostly carried out in the double-staged system (the Kawai-cell in the DIA apparatus) to extend experimental pressure. A whole geometry of the x-ray radiography system is shown in Figure 25. An x-ray

is introduced to the octahedral cell assembly through the gaps between the first- and second-stage anvils, and an x-ray once passed the cell illuminates a fluorescent YAG crystal. The visible light generated by the YAG crystal is transferred in the CCD camera where an image of the cell is captured. The system installed at beam line BL04B1 of SPring-8 can store 125 frames per second with a resolution of 2 μm per pixel. As the anvil gap of the Kawai-cell becomes narrow at high pressure, typically 1 mm at 10 GPa, fast acquisition of the images is essential to obtain accurate viscosity values, especially for a less viscous liquid such as Fe-alloy.

A typical falling sphere cell assembly is reproduced in Figure 26. A small sphere (100–150 μm diameter) of Pt, W,

or Au as a viscosity marker is put at the top of the sample. It should be noted that all the parts, except for the falling spheres and the sample, are made of matters of high x-ray transparency. After compression to the desired pressure, the sample is heated gradually to high temperature below the solidus, and then heated rapidly to the desired temperature above the liquidus. The cell assembly shown in Figure 26 was designed for viscosity measurement of Fe–FeS melts, in which two spheres are set in the sample capsule of h-BN, the first one at the top of the Fe–FeS powder and the second in the thin silicate layer set above the sample. The silicate possessing a melting temperature slightly higher than the sample is chosen so as to keep the second sphere in the silicate layer when the sample begins to



- ① First-stage anvil ② Second-stage anvil ③ Gasket ④ Pressure medium ⑤ Falling sphere
⑥ Sample ⑦ Fluorescent YAG ⑧ Mirror ⑨ Lens ⑩ CCD camera

Figure 25 A whole geometry of the x-ray radiography system (see text).

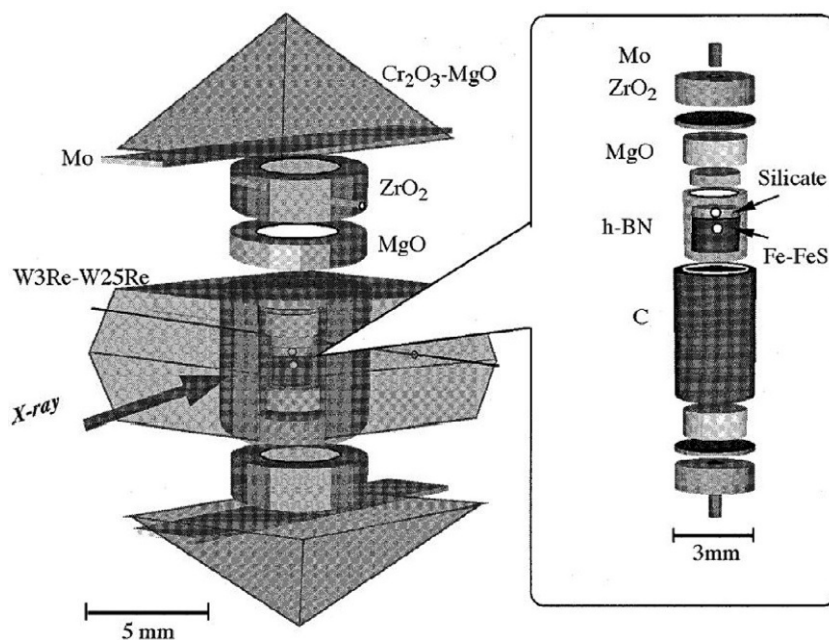


Figure 26 Schematic illustration of the falling sphere assembly (see Terasaki et al. (2001) for detail).

melt. Therefore viscosity data are collected at two different temperatures, corresponding to melting temperatures of the sample and the silicate in one experimental run (Terasaki et al., 2001). Similar methods were adopted in viscosity measurements of molten peridotite which has a relatively wide melting interval between solidus and liquidus and is sometimes difficult to define the 'settling velocity' to be transferred to the viscosity coefficient due to the coexistence of solid phases in the melt. Recently, a wide range of viscosities have been measured, for example, from orders of 10^2 Pa s (for alkaline silicates) to 10^{-2} – 10^{-3} Pa s (for Fe-alloy), over pressures up to 16 GPa.

The Kawai-cell composed of diamond/SiC composite cubes makes it possible to observe two-dimensional x-ray image and diffraction as well by combining with the first-stage anvils with wide conical slits. The system is suitable to examine the grain growth rate and the stress state under high P–T conditions.

2.10.4.7 Measurement of Elastic Wave Velocity Combined with In Situ x-Ray Observation Using SR

As mentioned in Section 2.10.1.1, an important goal of the high-pressure Earth sciences is to clarify the structure and chemistry of the Earth's interior based on the seismic velocity profiles, and, in this process, the elasticity of minerals, especially under high-pressure and high-temperature conditions, is indispensable. Ultrasonic measurement adopting the MAA is an appropriate method to obtain the elasticity under simultaneously controlled P–T conditions, in which elastic wave velocity is obtained by dividing the sample length by the travel time of the ultrasonic signal through the sample.

The pulse-echo-overlap method (Yoneda, 1990) and pulse-transmission method (Fujisawa, 1998) were combined with the Kawai-type apparatus in the last few decades, and the elasticity of MgO and MgAlO_4 up to 8 GPa and $\beta\text{-Mg}_2\text{SiO}_4$ up to 14 GPa, respectively. In these works, however, the piezoelectric transducer of LiNbO_3 was directly contacted to the sample and/or the buffer rod inside the solid pressure medium. Therefore, the deviatoric stress enhanced with pressure rapidly lowers the signal-to-noise ratio of the ultrasonic signal. Moreover, the experimental temperature is virtually limited to about half of the Curie temperature of the transducer (1523 K for LiNbO_3) (Turner et al., 1994).

These disadvantages were overcome by Li et al. (1996), who used a cubic WC anvil of the Kawai-cell as the buffer rod to transmit the ultrasonic signal to the sample and mounted the transducer onto the back truncated corner of the anvil. The ultrasonic interferometry in the MAA made remarkable progress by being coupled with in situ x-ray observation (x-ray diffraction and x-ray radiography) at the SR facility of the Brookhaven National Laboratory (e.g., Liebermann et al., 1998). It should be noted that the innovation has been carried out almost exclusively by researchers of SUNY at Stony Brook.

The whole system was also installed in the DIA type press SPEED-1500 at beam line BL04B1 of SPring-8 and applied to the Kawai-cell inside (Higo et al., 2009). Figure 27 shows a cross section of the typical constitution of the specimen assembly used for combined ultrasonic measurement and in situ x-ray observation at high pressures and high temperatures.

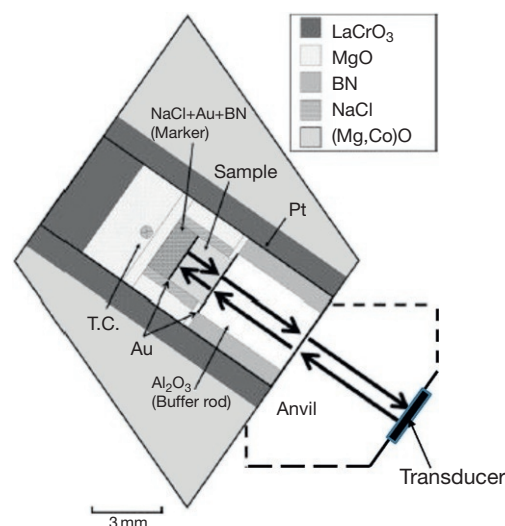


Figure 27 A cross section of the cell assembly used for elastic wave velocity measurement under high pressure and high temperature combined with in situ x-ray observation. The thick arrows indicate the propagation of the supersonic wave. Modified from Figure 2 of part in Higo Y, Kono Y, Inoue T, Irifune T, and Funakoshi K (2009) A system of measuring elastic wave velocity under high pressure and high temperature using a combination of ultrasonic measurement and the multi-anvil apparatus at SPring-8. *Journal of Synchrotron Radiation* 16: 762–768.

The 10° rotated Y-cut LiNbO_3 transducer, which can generate longitudinal and shear waves at the same time (Kung et al., 2002), is used to generate and receive the ultrasonic signals. The travel time is determined by the pulse-echo-overlap method for the reflected signals from the boundary between the buffer rod (Al_2O_3) and from the sample end. The x-ray image around the sample (Section 2.10.4.6) is recorded by a high-resolution CCD camera that is set immediately after the high-pressure apparatus. The sample length is directly observed from a distance between sharp dark lines of the thin Au foils set at the top and end of the sample which preferentially absorb x-rays compared to the buffer rod (Al_2O_3) and the sample. x-Ray diffraction is taken for both the pressure marker (NaCl and/or Au) and the sample. The former monitors experimental pressure and the latter gives in situ sample density. Temperature is monitored by the thermocouple. All these acquired data are basically sufficient to deduce elastic parameters of the bulk modulus K and the shear modulus G and their pressure and temperature derivatives over the measured P–T range. Higo et al. (2008) succeeded in precise measurements of sound velocities of ringwoodite at pressures to ~ 19 GPa and at temperatures to 1673 K. It is highly likely that pressure range of the elastic wave velocity measurement is largely extended by adopting SC cubes instead of WC cubes (Section 2.10.4.8).

2.10.4.8 Pressure Generation Using Sintered Diamond Anvil

As mentioned in Section 2.10.2.2, the capability of high-pressure generation of Kawai-type apparatus has been extended by using SD cubes instead of WC ones. In situ x-ray studies using the Kawai-cell equipped with SD anvils have been widely carried out to determine the phase equilibria (e.g., Irifune

et al., 2002; Ito et al., 2005, 2010a,b; Kubo et al. 2003; Ono et al., 2000; Tange, 2006; Yamazaki et al., 2011), to measure the electrical conductivity (Katsura et al., 2007), and to examine the spin transition (Ito et al., 2010a,b). Thanks to the extension of attainable pressure we could develop a few new pressure-fixed points up to ~ 60 GPa (see Table 1). Nevertheless, pressure calibration in the experiments at higher pressures inevitably relies on the in situ x-ray diffraction using the pressure standard materials. Recent performance of the pressure generation at 300 K is shown in Figure 28. SD cubes with 14 mm edge length

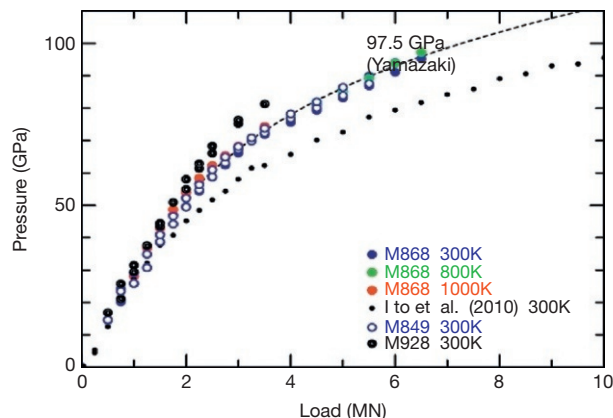


Figure 28 Results of pressure generation at 300 K for the Kawai-cell equipped with SD cubes with 14 mm edge length and 1.0 mm truncation (Ito et al., 2010a,b). An octahedral pressure medium of $\text{MgO} + 5\% \text{Cr}_2\text{O}_3$ with 4.1 mm edge length was employed. Variation of efficiency of pressure generation is due to the different setting of pre-gasket.

and 1.0 mm truncation were employed with an octahedral $\text{MgO} + 5\% \text{Cr}_2\text{O}_3$ pressure medium of 4.1 mm edge. The sample assembly was almost identical to that shown in Figure 21. The maximum attainable pressure is reaching 100 GPa.

2.10.5 New Applications

Two newly developed applications of the Kawai-type apparatus are briefly surveyed here. The first is the determination of rheological properties of mantle minerals at high pressure and temperature which was developed at CHiPR Stony Brook, USA. The stress and strain of the sample under nonhydrostatic conditions in the Kawai-cell are measured in situ using synchrotron x-ray. Schematic sample assembly is shown in Figure 29. The cylindrical sample is placed between the end plugs of hard corundum, and the sample length is measured from the radiographic images of the gold foils attached at the upper and lower ends of the sample. By using a classic image-processing algorithm (Li et al., 2003), a precision of the strain measurement is increased to 10^{-4} which makes a strain rate accurate to 10^{-7} to 10^{-6} depending on the time interval between two measurements.

The stress is measured by simultaneously collecting energy dispersive x-ray diffraction patterns of the sample in two perpendicular diffraction planes according to analytical method of lattice strain $\varepsilon(hkl)$ developed by Singh (1993) and Singh et al. (1998). In order to gain accessibility for diffracted x-rays, six of eight WC cubes are replaced by sintered cBN as shown in Figure 30. The Kawai-cell is compressed in a set of wedges of six split cylinders. Conical notches are made in the wedges to

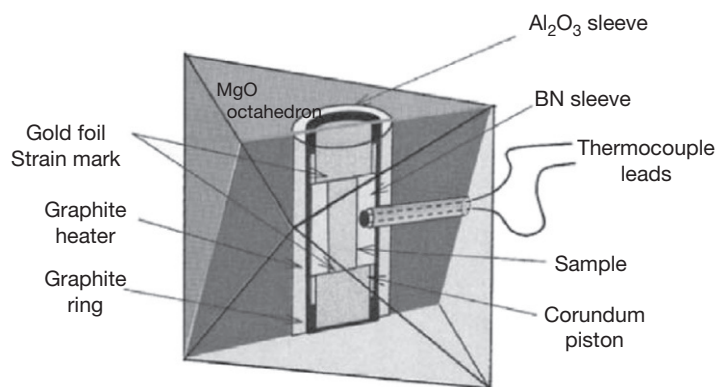


Figure 29 Cell assembly for high-pressure deformation experiments in the Kawai-cell (Chen et al., 2004).

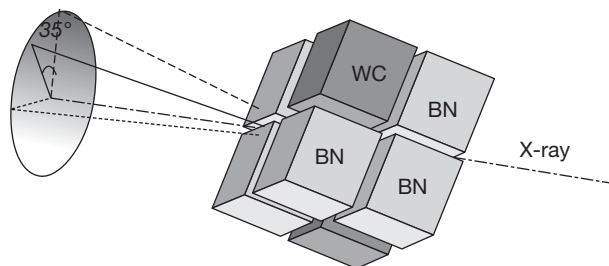


Figure 30 Diffraction geometry in Tcup module (see text) (Chen et al., 2004). Solid line indicates the access of diffracted x-ray if all eight cubes are made of WC, and brooked and dotted lines indicate the diffraction in vertical and horizontal planes penetrating through cBN side cubes, respectively.

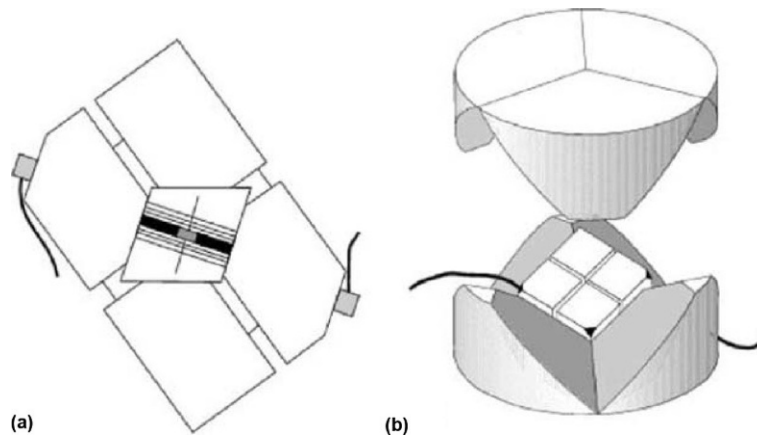


Figure 31 Schematic drawing of setup for AE measurement in the Kawai cell (Dobson et al., 2004). (a) Section of cell and anvil set showing acoustic wave guide (black) connecting the sample to the anvils with transducers mounted on the back. (b) Anvil set in the first-stage wedges.

ensure the path for diffracted x-rays. The whole system is named Tcup. Deformation experiments are carried out up to 10 GPa and higher than 1000 °C.

Another interesting new application of the Kawai apparatus is a combination with the acoustic emission (AE) technique performed by Dobson et al. (2004) to study the physical processes involved in seismogenesis. Their experimental setup is reproduced in Figure 31. AE transducers are mounted on truncations at the back of the furnace anvils. Acoustic waveguides (polycrystalline Al_2O_3 or Fe) are inserted between sample ends and the top truncations along the furnace axis to couple the sample to the furnace anvils. They carefully optimized the following factors essential to data acquisition: choice of waveguide material and appropriate length so that the sample is not crushed or faulted, electrical insulation of the AE transducers from the furnace anvils, and elimination of unwanted noise from sources outside the sample. As a proof of concept, Dobson et al. (2004) showed results from AE studies on antigorite dehydration to 8 GPa and the α - β transformation in San Carlos olivine at 16 GPa. Association of this method with in situ stress measurement using SR mentioned above will make it possible to determine the exact P-T- σ regime of brittle failure under extreme conditions (Dobson et al., 2004).

2.10.6 Future Perspectives

Future development of the MAAs will typically be in two directions: the generation of moderate pressure to 30 GPa over a large volume over 1 cm³ (e.g., Frost et al., 2004) and generation of pressures higher than 100 GPa (e.g., Ito et al., 2010a,b). The first is required to synthesize large crystals of materials composing the deep interior of the Earth. As already mentioned (Section 2.10.3.4), the crystals can be used to various kinds of measurements required to understanding the state of the mantle. Large sample volume, in turn, makes it possible to carry out these measurements under conditions deeper in the mantle. It is a great achievement to be able to determine qualitatively the state of the mantle and core materials under conditions up to the core-mantle boundary by extending accessible pressure.

It should be emphasized that in situ x-ray observation using SR has become an indispensable tool in the whole high-pressure

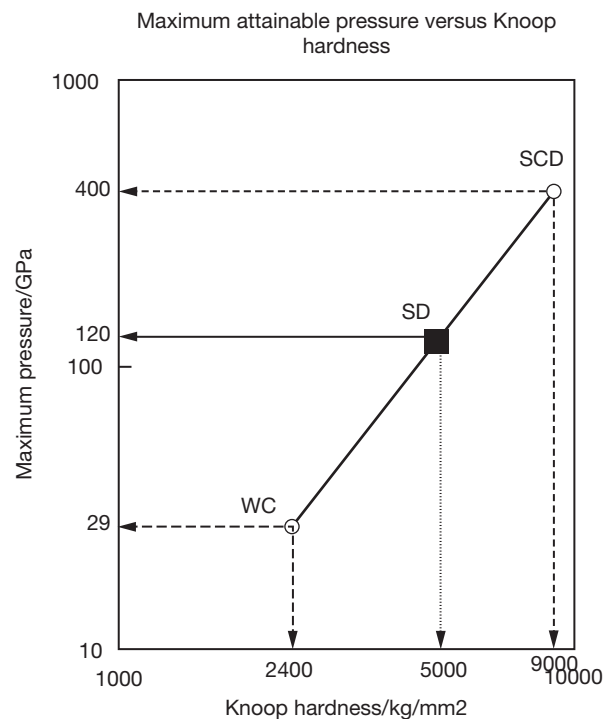


Figure 32 The log-log plot of the maximum attainable pressure by using WC and SCD versus Knoop hardness (Sung and Sung, 1996). The linear relationship indicates that generation of 120 GPa is possible by using SD anvils.

research. This technique not only offers the most reliable pressure values but also has developed research fields such as reaction kinetics of phase transformation, viscosity, and deformation measurements by means of x-ray radiography.

As mentioned in Section 2.10.2.2, usage of harder materials for anvils is essential to extend the maximum attainable pressure in the MAA. It is possible to generate 40 GPa in the Kawai-type apparatus by adopting specially improved WC (Katsura et al., unpublished data). In experiments at higher pressures, however, SD of Co-binder has been the most promising of anvil materials. In Figure 32, the maximum pressures attained so far are plotted against Knoop hardness (Sung and



Figure 33 The enlarged NPDs (Irifune et al., 2004). (a) As synthesized NPD cylinder with 10 mm diameter. (b) NPD cubes for the Kawai-cell. By courtesy of T. Irifune.

Sung, 1996) for WC (in the Kawai-type), and single-crystal diamond (SCD in DAC). According to the general trend, the Knoop hardness of SD suggests that pressures up to 120 GPa can be generated by adopting SD. In this connection, Irifune et al. (2004) synthesized new polycrystalline diamond pellets with grain sizes of 10–20 nm which is binderless and transparent. It is remarkable that the Knoop hardness of the pellet is up to 140 GPa, which is comparable or even higher than those of natural SCDs. The SD is named nano-polycrystalline diamond (NPD). Recently Irifune's group of Geodynamic Research Center (GRC), Ehime University, introduced a 6000 ton press (BOTCHAN-6000) to produce larger NPD. They have so far succeeded in making a cylindrical NPD with both diameter and length of 10 mm (Isobe et al., 2010), which is machined to a cubic anvil for the Kawai-cell as shown in Figure 33. The advent of such new SD material will make it possible to generate pressures of multi megabars using the MAA without reduction of the sample volume in near future.

A problem in experiments using the MAA is the occurrence of explosive extrusion of the pressure medium, blow-out, during compression, decompression, or heating, often causing damage of anvils and loss of the sample. The blow-out occurs in high frequency in experiments using SD cubes, which brings serious loss. There have been no effective measures to prevent the blow-out except slow compression and decompression and

adoption of a thin and wide pregasket. It is certain that the frequency of blow-out is lower in squeezing the Kawai-cell by the oil chamber system than in the solid guide block.

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2.11 Theory and Practice: Diamond-Anvil Cells and Probes for High- P - T Mineral Physics Studies

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2.11.1 Diamond-Anvil Cell as a Window to the Earth's Interior

With the rapid emergence of diamond-anvil cell (DAC) research as a major dimension in physical sciences, the literature is growing at an explosive rate. A comprehensive discussion of any one of the sections could easily fill a whole book. Therefore, our strategy is to introduce the essential concept for each subject, lay out the key background, and then jump to the latest activities on technical developments, mineral physical applications, current problems, and future prospects. Ample references are provided for readers who seek a deeper understanding of these topics.

2.11.1.1 Deep-Earth Geophysics and Geochemistry

By far, the major fraction of minerals in the solid Earth is hidden at great depth under high pressures (P) and temperatures (T). These minerals dictate the formation, evolution, present state, and destination of the planet. Recent geophysical and geochemical studies of the Earth's deep interior present us with a rich array of large-scale processes and phenomena that are not fully understood. These range from the fate of deeply subducting slabs; to the origin of plumes; to the nature of the core-mantle boundary layer; to the differentiation of elements to form the present-day crust, mantle, and core; to the distribution of trace elements; and to the uptake and recycling of

volatiles over the course of the Earth's history. Resolving these questions requires a detailed understanding of the chemistry of the relevant materials at high P - T . Under these extreme conditions, the physical and chemical behaviors of elements can be profoundly altered, causing new and unforeseen reactions to occur and giving rise to structural, elastic, electronic, and magnetic transitions not observed in mineral systems in the near-surface environment. This problem precludes attempts to understand the properties of materials at high P - T using our knowledge of minerals at ordinary conditions.

DAC provides the enabling tool for studying Earth materials at extreme conditions. Following its invention in 1959 (Weir et al., 1959), decades of development have extended the P - T range of the DAC so that it now covers conditions of the entire region spanned by the geotherms of the Earth and other terrestrial planets and significant portions of the Jovian planetary interiors (Figure 1). In addition, the excellent transparency of single-crystal diamond windows to a wide range of electromagnetic radiation has allowed the development of numerous analytic probes for comprehensive, in situ characterization of high P - T mineral properties.

2.11.1.2 Comprehensive High- P - T Mineral Properties

Knowledge of the key high- P - T mineral properties in the following nonexhaustive list is required for understanding deep-Earth geophysical and geochemical phenomena: composition; phase relation; melting curve; crystallographic structure; amorphous or liquid structure; crystallographic site occupancy, order-disorder, and defects; element partitioning; oxidation state; hydration/dehydration; density (ρ); aggregate bulk modulus (K); shear modulus (G); thermal expansivity (α); thermodynamic parameters (heat capacity at constant pressure or volume (C_p , C_v), Debye temperature (Θ_D), Grüneisen parameter (γ), entropy (S), energy (E), etc.); single-crystal elasticity (c_{ij} or s_{ij}); aggregate compressional-wave velocity (V_p) and shear-wave velocity (V_s); single-crystal V_p and v_s as a function of crystallographic orientation; phonon density of state (DOS);

phonon dispersion; preferred orientation under stress; shear strength and hardness; viscosity; diffusivity; creep law and deformation mechanism; thermal conductivity; radiative heat transfer; optical absorption; index of refraction; electric conductivity; dielectric parameter; and magnetism.

Owing to the often Herculean efforts in improving and developing experimental capabilities, all of these properties can now be investigated by DAC probes. Although researchers normally focus on at most a few properties as part of a well-defined study, they still need to maintain a comprehensive view of the entire suite of interrelated properties. Each geophysical problem may require knowledge of a host of properties, and each property may be applicable to a host of problems. Similarly, on the experimental side, each technique may provide information on a host of properties, and each property may be determined by a host of complementary techniques. Finally, the integrated high-pressure research impacts on multidisciplinary science and is shown in Figure 2.

The following example illustrates the integrated, interactive process that is at the heart of mineral physics and that shapes the development of experimental techniques for studying key materials properties that apply to Earth problems. The Earth's core plays a central role in the evolution and dynamic processes within the planet. However, answers to some of the most fundamental properties of core remain elusive (e.g., its temperature, chemical composition, crystalline phases, elasticity, and magnetism). As the major constituents of the core, iron and its alloys hold the key to answering these problems, and understanding their high- P - T behavior has been a focus of mineral physics since the seminal 1952 work of Francis Birch (Birch, 1952). In 1964, Taro Takahashi and William A. Bassett used x-ray diffraction (XRD) in the DAC to determine the high-pressure crystal structure of iron and discovered the hexagonal close-packed (h.c.p.) polymorph (Takahashi and Bassett, 1964). In the process, they also helped initiate what has become the extremely fruitful application of XRD in a DAC for mineral physics studies. Pioneering investigations of the iron melting curve with laser-heated DACs (Boehler, 1993;

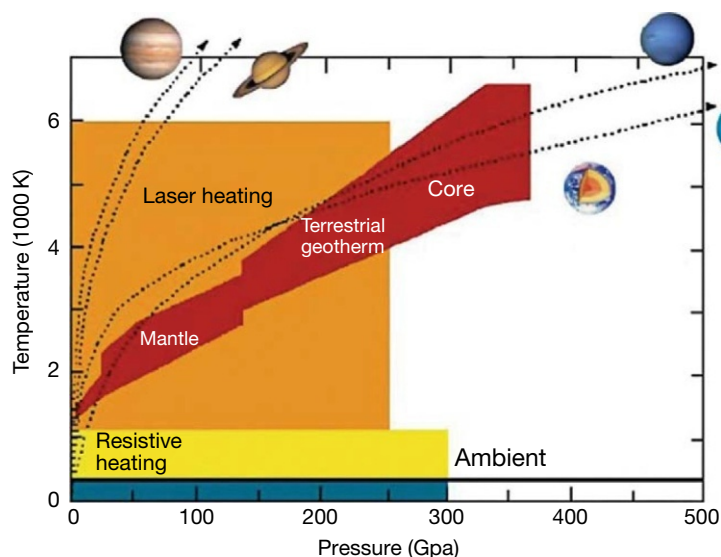


Figure 1 P - T range of diamond-anvil cell (DAC) techniques in comparison with conditions of planetary interiors.

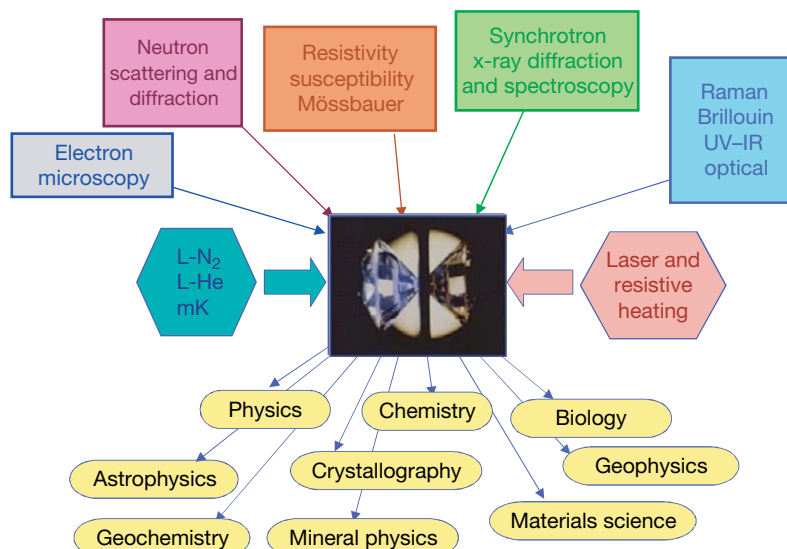


Figure 2 Integration of various analytic techniques for probing high-pressure samples in a DAC subjected to simultaneous high and low temperatures. The results impact on multidisciplinary scientific research.

Saxena et al., 1993; Williams et al., 1987) and the high-*P-T* iron phase diagram with simultaneous laser heating and synchrotron XRD (Andrault et al., 1997; Saxena et al., 1995; Yoo et al., 1995) have generated a great deal of excitement, as well as controversy (Anderson, 1997). This in turn has become a main driving force for advancement and improvement of these techniques. Indeed, the ‘mission to the Earth’s core’ (Stevenson, 2003) has united observational, theoretical, and experimental geophysics (Hemley and Mao, 2001a; Scandolo and Jeanloz, 2003) and enriched each discipline through interactions and feedback. Geophysical observations uncovered surprising inner-core properties such as seismic anisotropy, superrotation, and magnetism (Glatzmaier and Roberts, 1996; Niu and Wen, 2001; Romanowicz et al., 1996; Song and Helmberger, 1998; Song and Richards, 1996; Su et al., 1996). Geodynamicists proposed theories to interpret these observations (Buffett, 2000; Buffett and Wenk, 2001; Karato, 1999; Olson and Aurnou, 1999). Ab initio theoretical calculations (Alfé et al., 1999, 2000; Belonoshko et al., 2003; Laio et al., 2000; Steinle-Neumann et al., 2001; Stixrude and Cohen, 1995; Vocadlo et al., 2003) were applied to predict the melting, phase stability, elastic anisotropy, and magnetism of iron beyond experimental capabilities. Novel DAC techniques have been developed to overcome previous limitations and provide direct, experimental answers on the properties of high-*P-T* iron and iron alloys (Dubrovinsky et al., 2000; Fiquet et al., 2001; Lin et al., 2002; Mao et al., 1998b, 2001; Merkel et al., 2000; Wenk et al., 2000).

2.11.1.3 Multiple Radiation Probes

Unique advantages of the DAC as a static high-pressure apparatus include the maximum pressure attainable, as well as pressure accuracy, and most importantly the multitude of in situ analytic probes that can be used to study the DAC sample environment. Diamond is transparent to electromagnetic radiation from microwaves, the far infrared (IR), the visible (VIS),

and the ultraviolet (UV) up to the diamond bandgap at 5 eV. Diamond is opaque between 5 eV and soft x-rays up to 5 keV and is then transparent again to x-rays and γ -rays above 5 keV. Diamond is transparent to neutrons but opaque to other particles that require vacuum, such as electrons, ions, and protons. Nonpenetrating radiation between 5 eV and 5 keV, which requires vacuum and is therefore incompatible with the high-pressure environment, is restricted to ex situ studies of samples quenched from high-*P-T* environment or has to be replaced with equivalent probes, such as inelastic scattering.

When monochromatic optical (from IR to UV) or x-ray photons with frequency ν_L is scattered by the sample, most of the scattered photons keep the original frequency (elastic scattering), but some show peaks at frequencies shifted (inelastic scattering) by the addition or subtraction of ΔE , which is the energy difference between the excited and ground states of a specific vibrational or electronic transition of the sample, that is, $\nu = \nu_L - \Delta E$ (Stokes) or $\nu = \nu_L + \Delta E$ (anti-Stokes). Elastic scattering is used in XRD and optical imaging, reflection, and absorption spectroscopies. Inelastic scattering includes optical Raman and Brillouin spectroscopies and various phonon and electron x-ray spectroscopies. Together, these types of interactions between incident photons and the sample provide a broad range of tools for materials characterization.

Optical radiation, x-ray, and neutron radiation provide complementary probes. For instance, inelastic scattering of light (Brillouin spectroscopy), x-rays, and neutrons can all be used to study phonon dynamics; each technique has its unique merits and limitations. Optical DAC studies can be conducted with laboratory-scaled light sources, lasers, and spectrometers; state-of-the-art x-ray or neutron studies generally require synchrotron or neutron sources at large user facilities. Both optical and neutron radiations are low in energy ($\sim$ eV) and have high-energy resolution; x-rays are high in energy (>5 keV) and have low-energy resolution. x-Rays and neutrons have short wavelengths comparable to unit cell dimensions and thus access a large region of reciprocal space ($q = 4\pi \sin \theta / \lambda$, where θ is the

scattering angle and λ is the wavelength) to the Brillouin zone edge and beyond; optical radiation has much longer wavelengths and is thus limited to a very small range near $q=0$ at the Brillouin zone center. Optical radiation requires clear, colorless windows and can easily be scattered, refracted, or blocked by interfaces and minor amounts of dark impurities; x-rays can penetrate light-element (low Z number) anvils and gaskets regardless of interfaces and additional materials; neutrons have great penetration power through most materials. Optical and x-ray beams can be focused down to micrometer-sized spots for probing minute samples at ultra-high pressures; neutrons lag behind in microbeam development and are limited to $>100\text{ }\mu\text{m}$ -sized samples.

2.11.2 Generation and Characterization of High Pressures

2.11.2.1 Anvils and Axial Windows

Anvil devices (Figure 3) are used for reaching pressures of the mantle transition zone ($>13\text{ GPa}$) and higher. The anvil is a rigid body consisting of a small pressure-bearing tip on one end that expands to a large base at the other end. The force applied to the low-pressure base (table facet) of opposing anvils is transmitted directed to the small tip (culet facet) where the pressure intensification is inversely proportional to the culet/table area ratio, because pressure is defined as force per unit area. The maximum achievable pressures in an anvil device depend upon the anvil material and the anvil geometry. Colorless, defect-free gemstones are ideal anvil materials owing to their exceptional strength and window qualities. Maximum pressures of 16.7, 25.8, 52, and 300–550 GPa have been reported for cubic zirconia (Xu et al., 1996a), sapphire (Xu et al., 1996b), moissanite (Figure 3; Xu and Mao, 2000), and diamond anvils (Xu et al., 1986), respectively, in an opposing anvil geometry where the anvils can also act as axial windows (i.e., parallel to the compression axis).

If the anvils were truly rigid bodies, they would be capable of sample compression up to the fracture limit of the anvil. In practice, however, all anvils, including diamond, deform elastically and develop a cup (Figure 4) resembling the geometry of a 'toroidal cell' (Khvostantsev et al., 1977). The cupping increases with pressure; while this has the desirable effect of providing a larger space for the sample and a flatter pressure gradient, that also has an adverse effect in that eventually, the rims of the two anvils touch and the pressure ceases to rise with further increases of force. Despite this effect, flat-culet anvils have reached megabar pressures (100 GPa) in 1976 (Mao and Bell, 1976) and a maximum reported pressure of 140 GPa (Yagi and Akimoto, 1982). In order to extend the pressure limit, bevels or convex shapes are added to avoid the touching rim. Beveled anvils with the optimum center flat/outer circle ratio of 1:3–1:10 and a bevel angle of 8.5° can reach 200–300 GPa before the bevel flattens as shown by x-ray imaging experiments (Hemley et al., 1997) and finite-element calculations (Merkel et al., 1999).

In addition, the potential of the many exceptional properties of diamond is only partially expressed in natural specimens but can be optimized in synthetic processes. By varying chemical dopants in the laboratory, the electronic behavior of diamond can be altered from a wide-gap insulator, to a *p*-type or *n*-type semiconductor (Haenen et al., 2004; Suzuki et al., 2004; Tajani et al., 2004), to a superconductor (Ekimov et al., 2004). Ultrahigh-purity synthetic diamonds open clear optical windows to radiation from the UV to far IR for transmission and inelastic scattering studies with exceedingly low background. Isotopically pure synthetic diamonds provide the highest known thermal conductivity. Defect-free, synthetic, single-crystal diamonds (Sumiya et al., 2005) can achieve a level of perfection unmatched by natural diamonds rivaling perfect silicon single crystals. For diamond-anvil application, the apparent hardness and toughness limit the maximum pressures attainable and are therefore more important than the absolute hardness, which in practice is unreachable due to the weak cleavage (Brazhkin et al., 2004). Synthetic

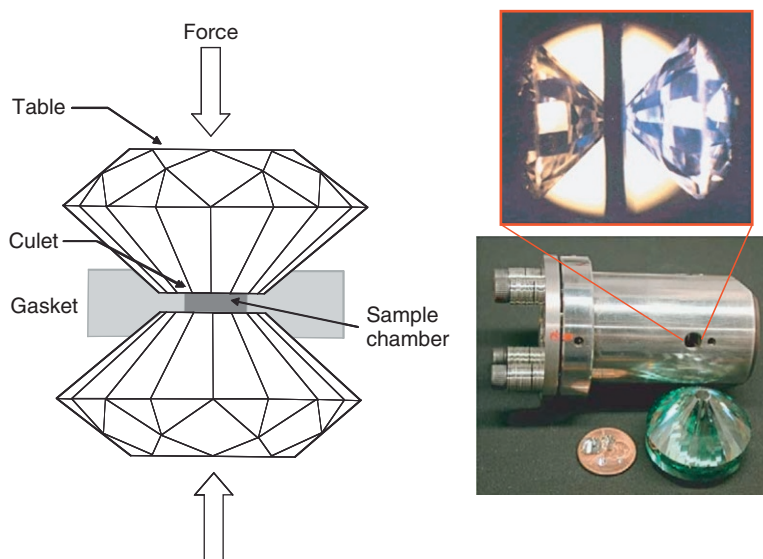


Figure 3 The principle of DAC. Bottom right, a large moissanite anvil is compared with the DAC.

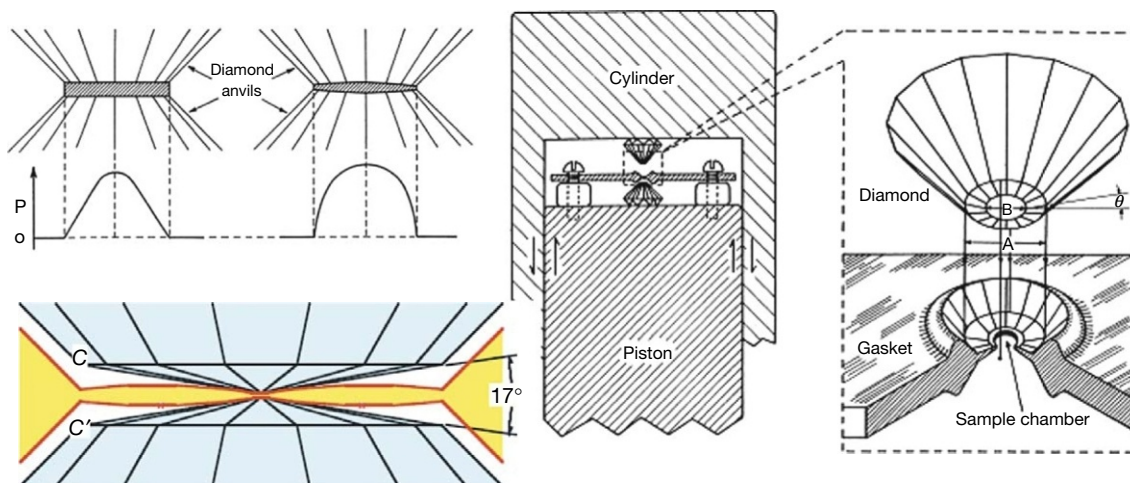


Figure 4 Top left, two flat culets compressing the gasket and producing the smoothly rising pressure profile underneath. Top second left, culets cupping under high pressures and producing sharply rising pressure gradient at rim. Bottom left, culets with 17° bevel angle flattened elastically when central pressure reached 300 GPa (Hemley et al., 1997). Center, diamonds aligned on piston and cylinder, which guide the compression on the gasket. Far right, details of the beveled diamond and indented gasket.

single-crystal (Yan et al., 2004) or polycrystalline diamonds (Irifune et al., 2003) with properly randomized defects that hamper the propagation of cleavage show greater apparent hardness and toughness than diamonds in which the strength is dictated by cleavage. Exploration of these properties may unleash the full power of diamond anvils and revolutionize the field of high-pressure experimental geophysics and geochemistry.

This exciting prospect has only been limited by our ability to synthesize sizable single-crystal diamond at affordable cost and within reasonable time. The cost and availability of natural single-crystal diamonds limit their anvil size to typically 0.25–0.3 ct (1 ct = 0.2 g) although the largest diamond used as an anvil was 4 ct (Glazkov et al., 1988). Two existing methods, high-pressure/high-temperature (HPHT) and chemical vapor deposition (CVD), have been used to grow single-crystal diamonds. The HPHT method is very expensive (more than natural single-crystal diamond) and slow and is practically limited to sizes of 2.5–3 ct. The CVD epitaxial process has been successfully used for overlaying circuits on anvil tips for electromagnetic measurements (Jackson et al., 2003, 2005a) and depositing isotopically pure ^{13}C as a pressure sensor (Qiu et al., 2006). The very rapid-growth CVD process (Yan et al., 2002) has produced diamond anvils that reached 200 GPa (Mao et al., 2003b) and a 10 ct-size single-crystal diamond (Ho et al., 2006) that could be used for two orders of magnitude larger samples than presently available at megabar pressures.

2.11.2.2 Gasket and Side Window

Gaskets in anvil devices serve four critical functions: (1) providing lateral support to protect anvil tips, (2) building a gradient from ambient to the peak pressure, (3) encapsulating the sample, and (4) providing an alternative window for x-ray and neutron probes. Outside the diamond culet area, the gasket forms a thick ring that supports the anvils like a belt, without which the anvils would not survive above

30–40 GPa. The effectiveness of the support depends on the tensile strength and thickness of the gasket. Between two parallel culets, the thin, flat portion of the gasket sustains a large pressure gradient from the minimum stress at the edge of the culet to the maximum stress at the center. The gasket thickness, t , does not depend upon its initial thickness but is rather a function of the shear strength of the material, σ , and the pressure gradient along the radius r , $\partial P/\partial r$ (Sung et al., 1977):

$$t = 2\sigma / (\partial P / \partial r) \quad [1]$$

Different materials are used as gaskets to optimize specific functions and experimental goals. Hardened steel is used as an all-purpose gasket material. High-strength rhenium is used for experiments requiring large thickness or high temperature. Composite gaskets can be constructed to optimize different functions at different parts of the gasket; for example, insulating inserts (MgO or Al_2O_3) are added to metallic gaskets for the introduction of electrical leads into the high-pressure region. Using a composite gasket that includes diamond powders or a diamond coating on the central flat region of the gasket greatly increases the shear strength and can increase the gasket thickness by two to three times (all other factors remaining constant) (Zou et al., 2001). Since the sample volume in a DAC is defined by the gasket thickness and the hole (sample chamber) diameter in the gasket, doubling the thickness of the sample chamber effectively doubles the sample volume. To eliminate the grain boundary fracture and to avoid interference of XRD patterns from high- Z crystalline gasket materials, high-strength bulk metallic glass has been used as a gasket to above 100 GPa (He et al., 2003). Sample reaction must also be carefully considered when choosing gaskets especially with highly reactive samples like hydrogen peroxide (Cynn et al., 1999).

x-Ray and neutron radiation can penetrate appropriate gasket materials and probe DAC samples in an equatorial or radial geometry (i.e., perpendicular to the compression axis) (Mao et al., 2001). The gasket materials are chosen for mechanical strength and transparency and low scattering background

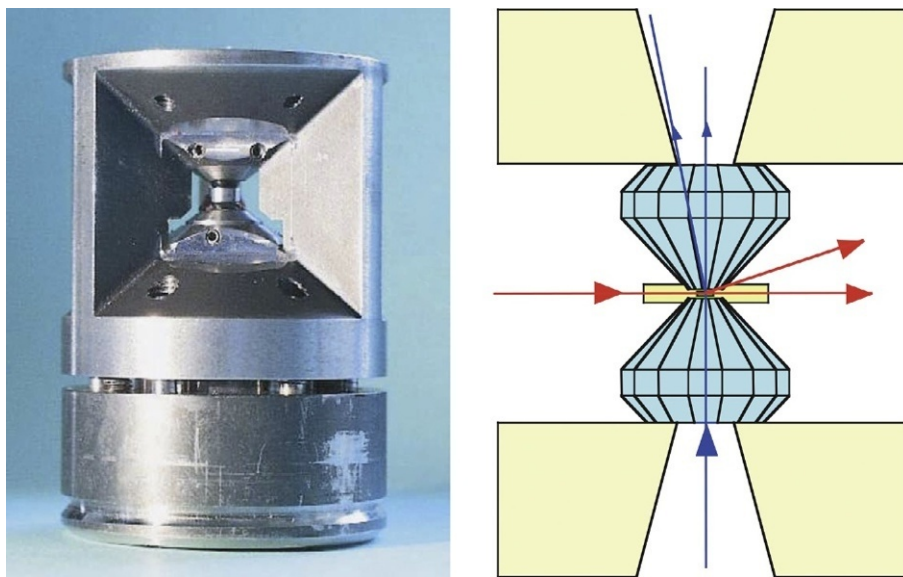


Figure 5 Panoramic DAC with Be gasket. The radial path has larger opening and is much less absorbing to the probing x-radiations than the axial path because of the low absorption coefficient of Be.

(Figure 5). For x-ray studies, high-strength beryllium (Mao et al., 1998b) (ultimate tensile strength, 517 MPa; microyield strength, 68.9 MPa), amorphous boron epoxy inserts (Lin et al., 2003b) with kapton belts (Merkel and Yagi, 2005), and compressed, superhard graphite (Mao et al., 2003a) inserts with beryllium belts (Mao et al., 2006c) have been used to reach megabar pressures. With mutually canceling neutron scattering factors and high strength, the $\text{Ti}_{52}/\text{Zr}_{48}$ zero scattering alloy is used as a DAC gasket for neutron diffraction (Ding et al., 2005).

2.11.2.3 Samples and Pressure Media

When a solid sample is surrounded by a fluid medium during compression, it is subjected to a hydrostatic pressure, that is, the stress is uniform in all directions. At sufficiently high pressures, all fluids solidify with liquid helium solidifying at the highest pressure of 11 GPa (Besson and Pinceaux, 1979). Pressure is then transmitted through solid media. Solids have finite strength and cause pressure anisotropy or nonhydrostaticity, which refers to directional deviatoric stress at a point, and pressure gradients or inhomogeneity, which refers to the variation of stress conditions at different points in the sample. It is often desirable to eliminate or to reduce the pressure anisotropy and inhomogeneity, and pressure media are chosen for their low strength and chemical inertness in relation to the sample. A mixture of methanol-ethanol is commonly used in the DAC as a fluid medium to 10 GPa (Piermarini et al., 1973) above which its strength rises sharply. Inert-gas solids are commonly used as pressure media to produce quasihydrostatic conditions up to 8 GPa in argon, 20 GPa in neon (Bell and Mao, 1981), and over 100 GPa in helium (Dewaele and Loubeyre, 2005; Loubeyre et al., 1996; Takemura and Singh, 2006).

Gas pressure media can be loaded by placing the entire DAC in a large gas pressure vessel with the sample in a slightly

opened gasket hole. The gas is pumped into the vessel to a nominal pressure of 200 MPa, which fills the DAC sample chamber, as well as the surroundings. A feedthrough mechanism is then used to close the DAC sample chamber and seal the sample in the gas medium inside the gasket. The high-pressure gas-loading method (Mills et al., 1980) has the advantage of being able to load gas mixtures without phase separation and low-melting temperature gases such as He, H_2 , and Ne, without trapping bubbles in the gasket, but uses a significant quantity of gas at high pressures that requires rigorous safety precautions. A simple alternative is to use liquid nitrogen cooling to liquefy gases inside the DAC. This method is used extensively for loading argon as a gas medium and has the advantage for loading expensive and rare gases in 'ml' quantities (e.g., ^{83}Kr ; Zhao et al., 2002). When properly quantified, experiments under deviatoric stress can provide rich additional information about strength, elasticity, and rheology that are unavailable with hydrostatic experiments. The uniaxial compression of a DAC is ideal for quantitative study of deviatoric stress at ultrahigh pressures (Singh et al., 1998a,b). With radial XRD, the incident x-rays are directed perpendicular to the compression axis (i.e., through the gasket), allowing for measurement of how the d-spacings vary with ϕ , the angle between scattering direction and the compression axis. The difference in d-spacings obtained from the $\phi = 0^\circ$ and $\phi = 90^\circ$ gives the deviatoric strain $Q = (d_{0^\circ} - d_{90^\circ})/3d_p$, where $d_p = (d_{0^\circ} + 2d_{90^\circ})/3$ is the d-spacing under hydrostatic pressure $\sigma_p = (\sigma_3 + 2\sigma_1)/3$, where σ_3 and σ_1 are axial and radial stresses, respectively. With the hydrostatic equation of state (EOS), these data can be used to determine the deviatoric stress $t = \sigma_1 - \sigma_3$. The maximum uniaxial stress t supported by a material is determined by its strength; that is, $t = \sigma_y = 2\tau$, where σ_y and τ are the yield and shear strengths of the material, respectively. It is often assumed in high-pressure experiments that $t = \sigma_y$; however, in general, t varies with sample environment, and the equality (von Mises condition) is true

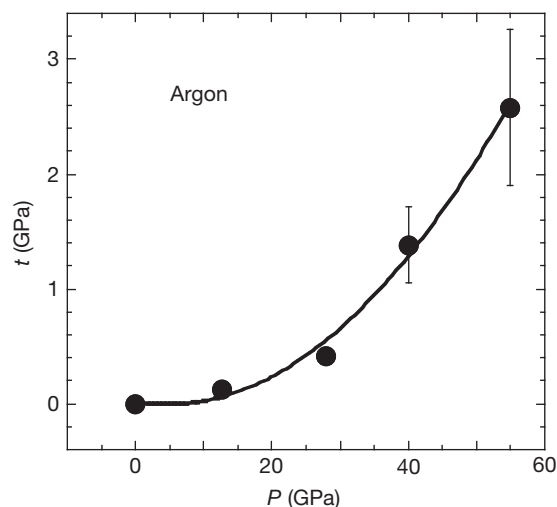


Figure 6 Deviatoric stress, which is the lower bound of the strength, of Ar as a function of pressure (reproduced from Mao HK, Badro J, Shu J, Hemley RJ, and Singh AK (2006) Strength, anisotropy and preferred orientation of solid argon at high pressures. *Journal of Physics: Condensed Matter* 18: S963–S968). The vertical bars indicate the range at different crystallographic orientations (*hkl*). The true error bars are significantly smaller.

only if the sample is observed to plastically deform under pressure. In [Figure 6](#) using this method, we demonstrated that the strength of argon could reach 2.7 GPa at 55 GPa ([Mao et al., 2006a](#)).

2.11.2.4 DAC Body

The main functions of the DAC body are to advance the anvils toward one another while allowing sample access to analytic probes. Dozens of DAC designs with different materials (most commonly hardened steel), sizes, shapes, aspect ratios, and openings of the DAC body have been devised to optimize for specific measurements at varying *P*-*T* conditions. For instance, cobalt-free steel is used to reduce neutron activation of the DAC, Be seats are used for single-crystal XRD, wide axial openings are used for Brillouin spectroscopy, and panoramic, radial openings are used for radial XRD, neutron diffraction, and x-ray spectroscopy (XRS) ([Figure 7](#)). High- ([Bassett, 2003](#)) or low-temperature ([Kawamura et al., 1985](#); [Pravica and Remmers, 2003](#); [Silvera and Wijngaarden, 1985](#)) alloys are used for DACs operated at extreme temperature conditions. Special nonmagnetic materials, including Be–Cu alloys ([Okuchi, 2004](#); [Timofeev et al., 2002](#)), plastics ([Matsuda et al., 2004](#)), and ceramics ([Yamamoto et al., 1991](#)), are used for making DACs for magnetic measurements. Miniature DACs less than 1 cm in size ([Eremets and Timofeev, 1992](#); [Mito et al., 2001](#); [Sterer et al., 1990](#); [Tozer, 1993](#)) have been developed to fit in the limited spaces defined by analytic probes, for example, in the 1 cm bore of the spindle for magic-angle-spin nuclear magnetic resonance studies ([Tozer, 2002](#)).

For operation in a moderate pressure range <10 GPa, the diamond alignment requirements are not critical, and the DAC design can be focused on ease of operation with maximum access for in situ probes (e.g., [Merrill and Bassett, 1974](#); [Oger](#)

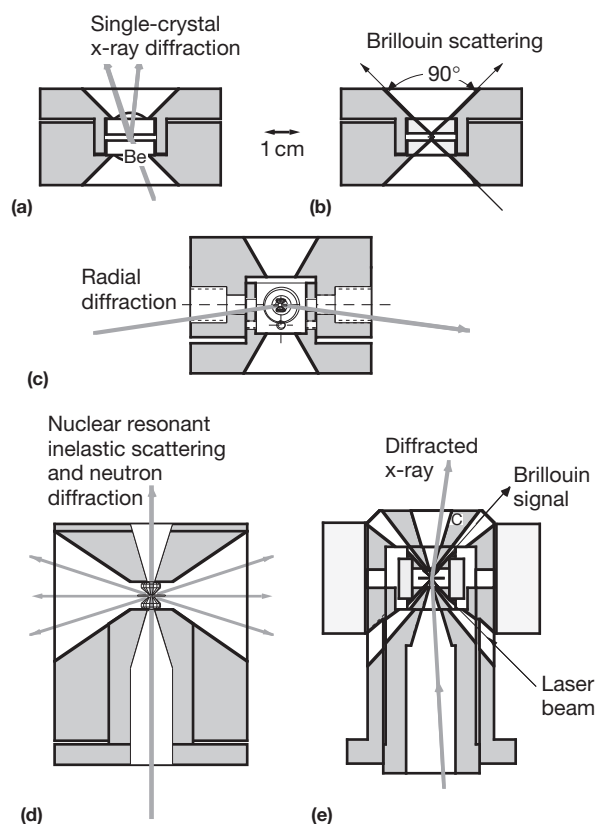


Figure 7 Various types of DAC optimized for specific functions as marked.

[et al., 2006](#)). For ultrahigh-pressure operation >30 GPa, preservation of the perfect alignment of the anvils during the compression process is absolutely crucial. To push the anvils together requires rigid, frictionless, linear displacement without wobbling or lateral shifting. This is accomplished by close fitting of the hardened steel piston and cylinder to mm accuracy ([Mao and Bell, 1976](#)). The same design principles are retained to keep the perfect alignment while maximizing optical and x-ray access through the axis in symmetrical DACs ([Mao et al., 1998a](#)) or through the radial directions in panoramic DACs ([Mao et al., 2001](#)).

The highest stress point of the body is at the table side of the two anvils, which are supported by high-strength seats made of tungsten carbide or cubic boron nitride (c-BN). Opposing diamond-anvil culets must be aligned to a lateral accuracy of 1–2% of the culet diameter and parallelism within 0.5–1 mrad. This alignment is achieved by two half-cylindrical seats (rockers) perpendicular to each other ([Mao and Bell, 1976](#)) or alternatively hemispheric and flat-disk seats, to provide two-dimensional tilt and translation alignment capability. More recent designs require manufacturing anvils, seats, and the DAC body to a parallelism of ± 0.5 –1 mrad. Then, tilt or rocking alignment is no longer necessary, and the rockers are simplified to two flat disks with only translational alignment ([Mao et al., 1994](#)). Seats made of another single-crystal diamond-backing plate ([Yamanaka et al., 2001](#)), conical seats that are supported at the conical side surrounding the table

(Boehler and De Hantsetters, 2004), and a combination of the conical seat and diamond-backing plate (Krauss et al., 2005) have been used successfully to reach high pressures while maintaining very large axial openings.

2.11.2.5 Compression Mechanism

Diamond anvils are typically compressed mechanically by screws and springs directly or with an additional lever-arm arrangement (Mao et al., 1994) or pneumatically by a diaphragm (Daniels and Ryschkewitsch, 1983) or membrane (LeToullec et al., 1992). Relative to a pneumatic system, the mechanical screw-spring system has the advantages of (1) stability (a cell has been kept at constant pressure at 200 GPa since 1986) without the concern of gas leak, (2) ease of transportation under high pressures, (3) low-temperature operation unlimited by the freezing point of the pneumatic gas, (4) accommodating large displacement without rupture of membrane, and (5) simplicity and low cost without the attachment of gas bottle and control. A pneumatically controlled membrane, on the other hand, has the advantages of remote and quantitative control of force increment without having to dismount or disturb the DAC.

Another option for remote pressure increment is the attachment of a motor-driven gearbox to a mechanical screw-spring system (Figure 8). A motor-driven DAC was used to increase pressure remotely up to 230 GPa while taking XRD patterns in 1–2 GPa steps. 142 XRD patterns were collected over 3 h demonstrating not only the efficient pressure change possible but also the potential for fine pressure and temporal resolution (Mao and Mao, 2006). Besides providing detailed *P*-*V* EOS measurements, this type, motor-driven DAC, could find application for time-dependent strain measurements and for experiments that require precise pressure resolution.

2.11.2.6 Pressure Calibration

For pressures above several GPa, the only viable primary pressure standard is the pressure-volume (*P*-*V*) EOS, which can be derived from independent determination of a pair of EOS parameters. In shock-wave measurements, the pair of variables are particle velocity (U_p) and shock velocity (U_s), from which the pressure-density relations are calculated. Such direct determinations of pressure are called primary standards. Once calibrated against a primary standard, any other pressure-dependent variable can be used as a secondary standard for pressure determination. Secondary standards are chosen for their accessibility and resolution. For the widely used 'ruby scale,' tiny ruby grains are added in the sample chamber (Piermarini et al., 1975), and the pressure shift of the ruby fluorescence wavelength can be easily probed with a laser beam through the diamond windows. The ruby scale has been calibrated against shock-wave primary standards of Ag, Cu, Mo, and Pd without a pressure medium up to 100 GPa (Mao et al., 1978) and against Ag and Cu in an argon pressure medium up to 80 GPa with $\pm 6\%$ uncertainty in pressure (Mao et al., 1986). With the improvement of XRD accuracy, the precision of pressure determination from each of the six primary standards, that is, Al, Au, Cu, Pt, Ta, and W, was greatly improved (Chijioke et al., 2005; Dewaele et al., 2004), but the spread of pressures determined from different standards is still as large as 6%, reflecting the need for improving the primary scale.

With improvements in spectroscopic techniques, the precision of ruby measurements and other secondary scales can now resolve 0.2–1% in pressure, but the shock-wave primary calibration that they rely on still carry a 5% uncertainty in pressure, which becomes the limiting factor for accuracy. Recently, a new pair of variables has been chosen to improve the accuracy of pressure calibration for anvil devices. They are

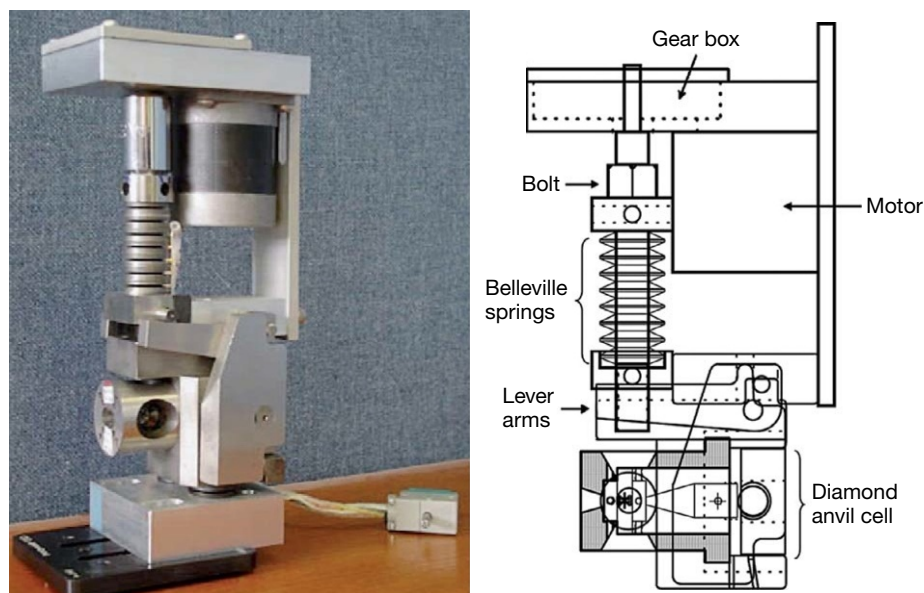


Figure 8 Motorized lever-arm DAC assembly. Left, picture. Right, mechanical drawing. Reproduced from Mao WL and Mao HK (2006) Ultrahigh-pressure experiment with a motor-driven diamond anvil cell. *Journal of Physics: Condensed Matter* 18: S1069–S1073.

the density (ρ) measured with XRD and the acoustic velocity (V_ϕ) measured with the ultrasonic method or Brillouin scattering on the same sample under the same compression conditions (Mao and Hemley, 1996). Pressure is derived directly by

$$P = \int V_\phi^2 d\rho \quad [2]$$

The resultant P - ρ relation is a primary pressure standard. Such measurements have been carried out on the MgO pressure standard in a helium pressure medium as a primary standard (Figure 9(a)), which was used for calibration the following ruby scale with 1% pressure accuracy up to 55 GPa at ambient temperature (Zha et al., 2000, 2004):

$$P \text{ (GPa)} = (A/B) \left\{ [1 + (\Delta\lambda/\lambda_0)]^B - 1 \right\} \quad [3]$$

where $A = 1904$ GPa, $B = 7.715$, and $\Delta\lambda$ is the ruby fluorescence wavelength shift from its ambient pressure value λ_0 (Figure 9(b)).

In summary, the present pressure calibration is robust to ± 6 –10% accuracy. A high-pressure community effort is underway to improve the primary calibration by improving the shock-wave equations of state, ab initio calculations, or simultaneous measurements of ρ and V_ϕ at higher pressures and temperatures. In DAC, ρ can be determined by XRD to an accuracy of 0.2%, and V_ϕ can be determined by single-crystal Brillouin spectroscopy (Section 2.11.4.4), impulsive stimulated light scattering (ISLS) (Section 2.11.4.4), or phonon inelastic XRS (Section 2.11.5.9) to an accuracy of 1%. Secondary scales based on XRD and optical spectroscopy (e.g., Raman shift of c-BN; Goncharov et al., 2005) are pursued for the goal of 1% accuracy and precision in pressure with the propagation of errors from various sources.

2.11.3 Temperature

2.11.3.1 Resistive Heating

XRD up to 1100 K and 100 GPa has been measured using electrical resistance coils external to the diamond anvils (Fei and

Mao, 1994; Figure 10). The P - T conditions with external resistance heating are well defined. The singularly high thermal conductivity of diamond results in temperature variations within the sample chamber that are typically less than ± 1 K. However, stress-bearing components, including the sample gasket, diamonds, diamond seats, and a portion of the DAC body, are also heated, which limits the maximum temperature for resistive heating to 1500 K due to softening of these components at high temperatures. Inert and reducing gases, such as argon with 5% H_2 , are used to avoid oxidization of the diamonds and metallic gasket. Systematic studies of P - V - T EOS and phase transitions of mantle minerals have been carried out with external resistive heating and simultaneous XRD over a wide P - T range. External resistive-heating techniques have been also applied to DAC research in physics, chemistry, and materials science, for example, Degtyareva et al. (2005) and Gregoryanz et al. (2005). Over a lower pressure range, external resistive heating of the DAC has been used extensively for a full range of optical and XRD and spectroscopy studies of hydrothermal fluids and solid (Anderson et al., 2002; Bassett, 2003; Bassett et al., 1993).

To minimize heating of DAC components and concentrate heating closer to the sample, the gasket (Dubrovinsky et al., 1997, 2000) or the diamonds (Burchard et al., 2003) can be used as the resistive heaters. Even closer to the sample, internal resistive heaters have been developed inside the DAC gasket chamber. For electrically conductive samples, the heater can be the sample itself. For instance, iron wire or foil of 5–20 μm size has been heated by passing electric currents up to its melting temperatures for determination of melting and phase transitions (Liu and Bassett, 1975; Mao et al., 1987a). For insulating samples, a metallic wire placed inside the gasket has been successfully used as an internal heater for heating the silica sample in the tiny hole in the wire for Raman spectroscopic studies up to 3000 K at 10 GPa (Zha and Bassett, 2003).

2.11.3.2 Laser Heating

Temperatures in excess of 5000 K (Weathers and Bassett, 1987) can be achieved for samples under pressure in DACs by heating

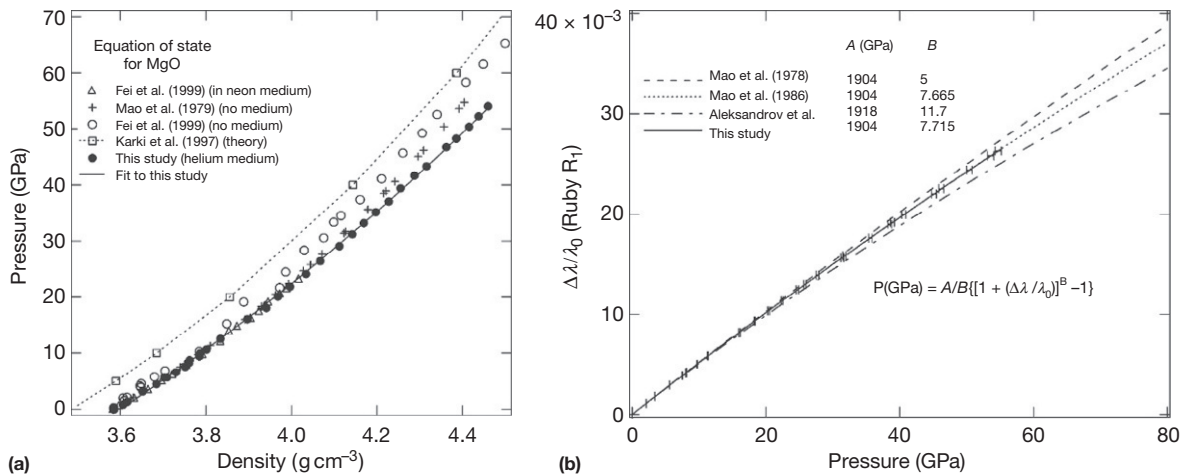


Figure 9 (a) The primary pressure standard of P - ρ equation of state of MgO obtained from x-ray diffraction determination of ρ and single-crystal Brillouin spectroscopy measurements of V_ϕ . (b) The secondary ruby scale based on the MgO standard. Reproduced from Zha C-S, Mao HK, and Hemley RJ (2000) Elasticity of MgO and a primary pressure scale to 55 GPa. *Proceedings of the National Academy of Sciences* 97: 13494–13499.

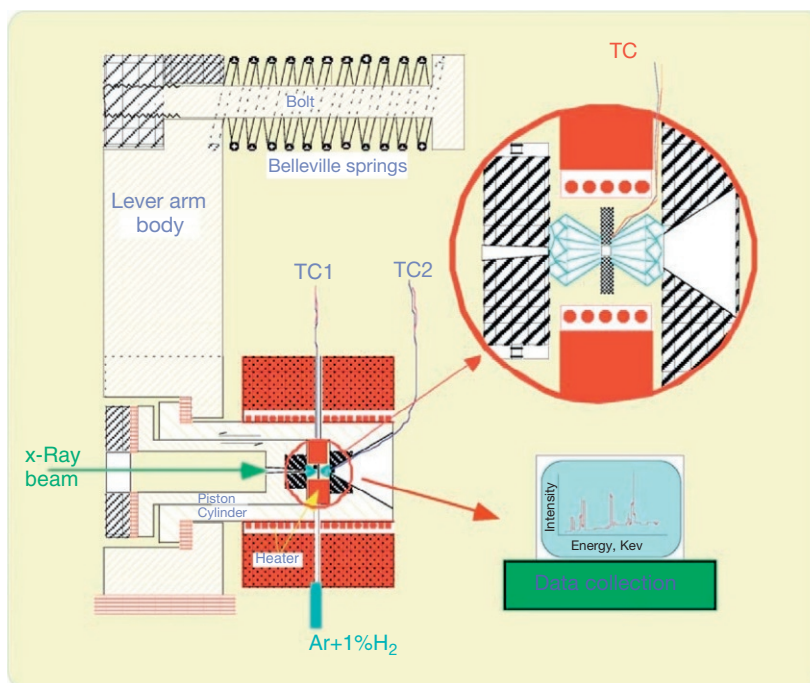


Figure 10 External resistive heating of a DAC with lever arms.

with high-power IR lasers (Bassett, 2001; Ming and Bassett, 1974). Due to the transient nature of laser heating (LH) and the steep temperature gradients (from the maximum temperature to ambient over 20 μm radial distance and even steeper axial gradients), in the past, contradictory results have been reported by different laboratories, causing confusion about the LH technique. Recently, significant progress in shaping and defining the temperature distribution in LHDACs has been made. With a 'double hot-plate' system, which exploits optimal laser characteristics, sample configuration, and optical arrangement, the LH method is approaching the accuracy of other high-*P*-*T* techniques using internal heaters. In this method, a multimode yttrium-aluminum garnet (YAG) laser, typically 20–100 W total power, provides a flat-top power distribution at the focal spot (Mao et al., 1998a; Shen et al., 1996). The method is further improved by the mixing of two yttrium lithium fluoride (YLF) lasers in TEM₀₀ and two in TEM₀₁ modes, to create a flat temperature distribution better than 1%. A hot-plate configuration is created when the heat generation and temperature measurement are concentrated at the planar interface of an opaque sample layer and transparent medium. The heating laser is split into two beams that pass through the opposing diamond anvils to heat the high-pressure sample simultaneously from both sides. The axial temperature gradient in the sample layer in the DAC is eliminated within the cavity of the two parallel hot plates. Variations of double-sided LH systems have been integrated with most synchrotron DAC beamlines (Liu et al., 2005; Schultz et al., 2005; Shen et al., 2001; Watanuki et al., 2001) for in situ x-ray studies at simultaneous high *P*-*T* (Figure 11). These systems have led to major discoveries of new lower-mantle phases (Kuwayama et al., 2005; Mao et al., 2006; Murakami et al., 2004).

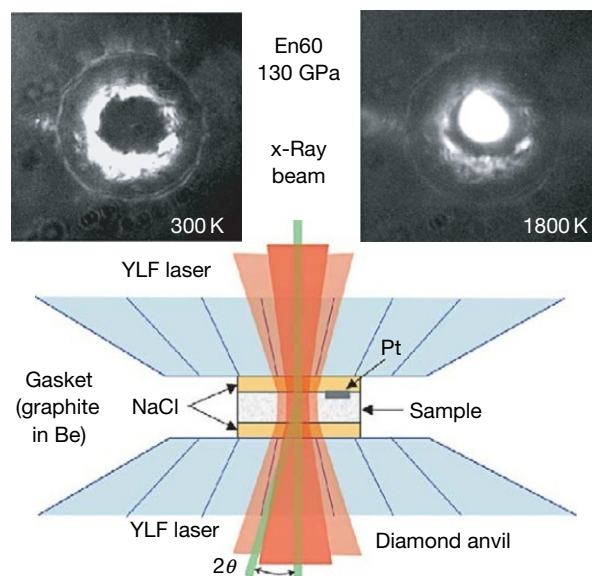


Figure 11 Left bottom, schematic of a laser-heated DAC. Top left, photomicrograph showing the $\text{Mg}_{0.6}\text{Fe}_{0.4}\text{SiO}_3$ orthopyroxene sample (En60) in a transparent graphite ring in Be gasket at 130 GPa before heating; top right, during laser heating to 1800 K.

The LHDAC technique requires an opaque, laser-absorbing sample and does not couple with transparent samples. This problem has been overcome for solid samples by mixing inert laser absorbers or for fluid samples by using a metallic foil with a high melting point (Pt, Re, or W of 5–15 μm in thickness) as the laser absorber, which in effect turns into an internal furnace (Lin et al., 2004b). A small 10–20 μm diameter hole is drilled into the foil, which is placed inside a gasket chamber filled

with the transparent samples and then compressed to high pressures (Figure 2). A YLF laser beam of 30 mm in diameter is centered at the hole and heats the peripheral metal foil around the small hole; the heated part forms a doughnut-shaped furnace effectively heating the transparent sample inside. Transparent samples such as CO₂ have been heated up to 1600 K and 65 GPa, indicating the high heating efficiency of the internal doughnut furnace method.

The progress of LHDAC has been marked by waves of breakthroughs and debates and is a good example of the general progress of most DAC techniques. The first application of Ming-Bassett LH technique for determination of Fe melting temperature at the core conditions (Williams et al., 1987) generated a great deal of excitement. It was followed by the well-known debate that (Boehler, 1993) reported much lower melting temperatures with LHDAC. In 1995, the Royal Society of London workshop was organized to discuss detailed problems on temperature gradients, temperature measurements, optical aberrations, and melting criteria that resulted in a comprehensive symposium volume (see Jephcoat and Besedin, 1996). The problems were mostly eliminated by subsequent development of new techniques. For instance, double-sided LH with flat-top power profile was developed to eliminate the temperature gradient (Shen et al., 1996), and in situ XRD was developed for positive identification of phases (Saxena et al., 1995; Yoo et al., 1995). These techniques were further refined, and in 2000, another community workshop was organized to discuss these advances in LHDAC (see Shen et al., 2001). General consensus for iron melting has been reached to at least 100 GPa (Ma et al., 2004). However, many readers may still only be aware of the debate a decade ago. Most recently, high-power fiber lasers with much higher power (100–1500 W) and superior stability, collimation, and flexibility have become available. This new capability will certainly revolutionize the LHDAC technique by lifting it to the next level of accuracy and performance.

2.11.3.3 Cryogenic

Experiments at simultaneous high-pressure and low-temperature conditions have less direct relevance for deep-Earth behavior but are important for understanding icy bodies. Fundamental understanding of high-pressure mineral physics, as well as constraints for theoretical studies, requires cryogenic studies of low-temperature phenomena. In principle, the use of high-pressure instrumentation does not affect the lowest temperatures possible for simultaneous high-pressure, low-temperature studies.

Cryogenic temperature, high-pressure conditions are created by cooling the entire DAC in a liquid nitrogen or helium flow cryostat, which is specially designed for pressure changes through long-stem wrenches for lever-arm-driven DAC or gas-line feedthrough for membrane DAC. The cryostat is designed with feedthrough circuits for electromagnetic measurements and windows for IR, optical Raman, and x-ray probes (Figure 12). Temperatures down to 4.2 K have been routinely reached at multimegabar pressures (Eremets et al., 2001b; Goncharov et al., 2001; Struzhkin et al., 2002), with a record low temperature of 27 mK being reached in a dilution refrigerator (Eremets et al., 2000).

The cryogenic DAC has been used extensively for simulating interior conditions of icy satellites in studies of multiple phases

of crystalline and amorphous ices (Cai et al., 2005; Yoshimura et al., 2006a,b), clathrates (Mao et al., 2002), and simple molecular compounds (Mao et al., 2005b). The high-pressure, low-temperature study of the Earth and planetary metals (Shimizu et al., 2001), gases (Eremets et al., 2001a; Goncharov et al., 2001; Loubeyre et al., 1993), and ices also provides the fundamental mineral physics basis for understanding theories and predictions of their behaviors at extreme high-*P-T* conditions. In addition, the cryogenic DAC is an important tool for low-temperature physics especially for novel superconductivities (Eremets et al., 2001b; Hemley and Mao, 2001b; Shimizu et al., 2002; Struzhkin et al., 1997, 2002).

2.11.3.4 Temperature Measurement

For external resistive-heating or cryogenic experiments, a large portion of the DAC is heated or cooled to a uniform temperature that can be simply measured by attaching thermocouples at strategic spots on or near the diamonds. For internal resistive-heating or laser-heating experiments, the temperature gradient can be very steep, and the peak temperatures are determined by noncontact, optical pyrometers with mm resolution. Optical probes through the strained, highly dispersive diamond windows often suffer from chromatic aberration, spherical aberration, and astigmatism that introduce errors and controversies in determination of temperature on the steep temperature gradient slope. Fortunately, the problems diminish in regions where the gradients are small. Therefore, the double-sided laser-heating method with flat-top power distribution (from either multimode or controlled mixture of TEM₀₀ and TEM₀₁ doughnut modes) has been developed to create a uniformly heated area at the peak temperature.

The accuracy and precision of temperature measurements in the laser-heated DAC have improved significantly with the use of spectral radiometry system (Shen et al., 2001). The thermal radiation spectrum is fit to the Planck radiation function to determine the temperature:

$$I_{\lambda} = c_1 \varepsilon_{\lambda} \lambda^{-5} [\exp(1 - c_2/\lambda T)] \quad [4]$$

where I_{λ} is spectral intensity, λ wavelength, ε_{λ} emissivity, and two constants $c_1 = 2\pi hc^2 = 3.7418 \times 10^{-16} \text{ W m}^2$ and $c_2 = hc/k = 0.014388 \text{ mK}$, where h is the Planck constant, c speed of light, and k the Boltzmann constant. The system response is calibrated by a tungsten ribbon lamp with a known relationship between radiance and power setting based on National Institute of Standards and Technology standards. Temperatures on two sides are measured separately with an imaging spectrograph and CCD and equalized by controlling the ratio of beam splitting. Above 1500 K, the use of blackbody spectral radiometry for primary temperature calibration is intrinsically superior to the use of a thermocouple, which is a secondary calibration and is affected by the stress effect on the electromotive force (EMF) and contaminants (Mao et al., 1971). In addition, the spectral radiometry measurements provide a real-time nonintrusive probe of continuous temperature profile, while thermocouples provide an intrusive point measurement. Uniform temperatures of 3000 K (± 20 K) have been achieved in a high-pressure sample of 15 mm diameter $\times$ 10 μm thickness. A significantly finer x-ray microprobe

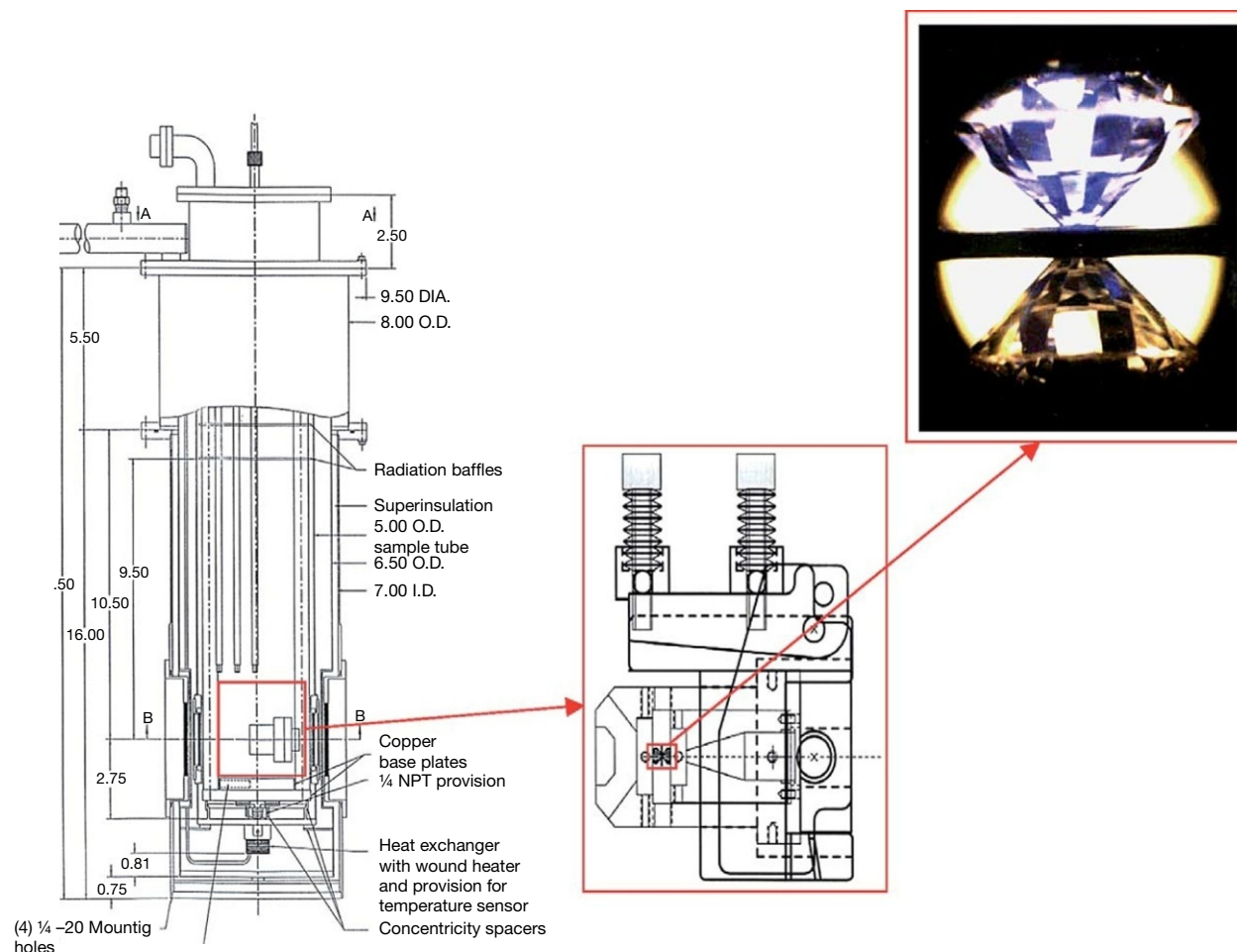


Figure 12 Liquid helium cryostat for high-pressure x-ray diffraction, x-ray Raman, and optical spectroscopic studies of gases, ices, and clathrates down to 4 K.

beam has been used for in situ characterization of the sample at these uniform *P-T* conditions. For example, phase relations and melting of iron and FeO have been studied at high-*P-T* conditions of the Earth's geotherm (Lin et al., 2003a). Measurements of FeO to 2200 K and 90 GPa show that the (subsolidus) boundary between the B1 (NaCl structure) and the metallic B8 (NiAs structure) phases has a significant positive slope.

A major source of error in spectral radiometry is the uncertainty of the emissivity, which is sample-dependent and has rarely been characterized as a function of wavelength and pressure (Benedetti and Loubeyre, 2004). The problem is especially severe for transparent samples, which have very low emissivities and are far from being ideal black bodies. Another optical probe has been developed for temperature determination of transparent samples from the intensity ratios of the anti-Stokes/Stokes excitation pairs of Raman spectra (Lin et al., 2004b; Santoro et al., 2004). The Stokes and anti-Stokes peak intensities are proportional to the populations in the ground and excited states, respectively, and thus depend on the temperature according to the Boltzmann distribution:

$$I_A/I_S = (v_A/v_S)^4 [\exp(\Delta v/kT)] \quad [5]$$

where I_A and I_S are the measured intensities of the anti-Stokes and Stokes peaks, respectively, v_A and v_S are the frequencies of

the anti-Stokes and Stokes peaks, respectively, and Δv is the relative Raman shift of the Stokes peak from the excitation laser frequency. In situ Raman spectroscopy by laser heating represents a powerful technique for characterizing high-*P-T* properties of molecular compounds present in planetary interiors (Lin et al., 2004b; Santoro et al., 2004).

The principle of using the Boltzmann distribution and anti-Stokes/Stokes ratio for temperature determination works regardless of whether the excitation photon is in the sub-eV optical range or in the 10 keV x-ray range. The anti-Stokes and Stokes sides of the phonon excitation spectra of a laser-heated ^{57}Fe sample in a laser-heated DAC were obtained with nuclear resonant inelastic x-ray scattering (NRIXS) spectroscopy yielding accurate, independent, temperature determination up to 1700 K at 73 GPa (Lin et al., 2004c).

2.11.4 Optical Probes

Through focusing microscope lens, the clear, colorless, single-crystal diamond windows allow many optical measurements with different geometries.

Figure 13 shows a generic high-pressure microspectrometer: transmission (or absorption) spectroscopy conducted by

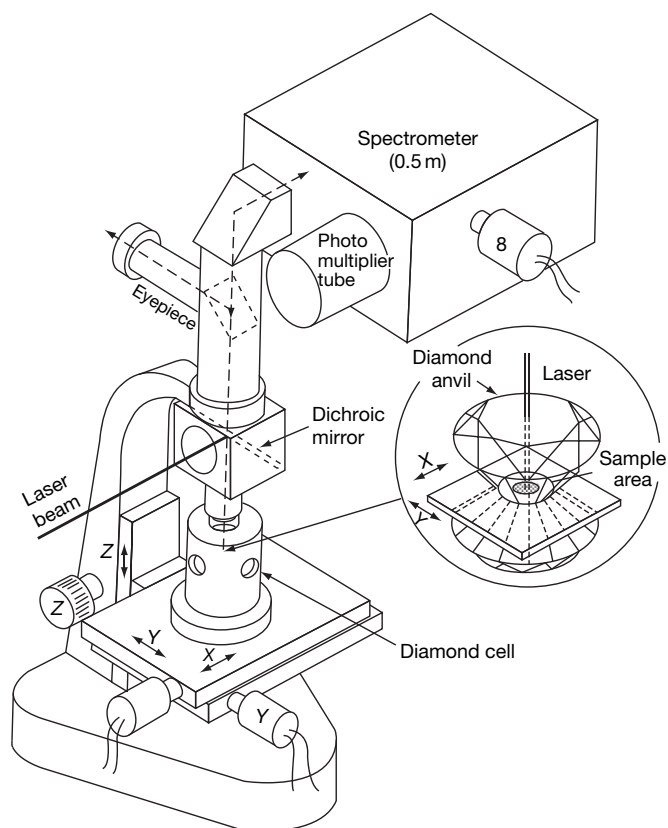
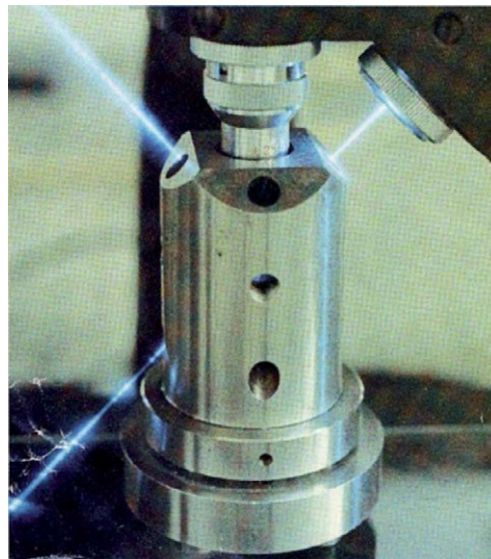


Figure 13 Optical system for DAC.

focusing the light beam from the bottom through the sample and received by the top microscope lens; reflective, Raman and fluorescence spectroscopy, with incident beam through the top lens and scattered beam back through the same lens; and Brillouin spectroscopy, with the two beams at a fixed angle. The scattered beam is collected and analyzed by the corresponding spectrometers. Although the details vary slightly, this universal approach has been adopted for many decades in DAC research.

2.11.4.1 Optical Absorption

Between the UV and IR regions of the electromagnetic spectrum, the color of minerals reveals a wealth of physical and chemical information. The optical appearance of ‘colorful’ minerals changes as the underlying properties are altered under pressure. These changes can be monitored through a modified transmission and reflectance polarizing microscope and analyzed by spectrometers. High-pressure melting, crystallization, and phase transitions can often be identified visually by movements of grain boundaries and changes of reflectivity, textural, morphology, and refractive indices (Bassett and Takahashi, 1965; Mao et al., 2006b; Takahashi and Bassett, 1964). High-pressure dielectric properties are determined from measurements of refractive indices with optical interferometry (Hemley et al., 1991). High-pressure changes of single-crystal symmetry are revealed by birefringence under crossed polarization or distortion of shape and interfacial angles (Yagi et al., 1979). High-pressure metal-insulator transitions also show conductivity changes in optical range; for example, at



the aforementioned pressure-induced transition of graphite to an insulating state, the graphite sample becomes transparent (Hanfland and Syassen, 1989; Utsumi and Yagi, 1991). Pressure-induced changes of optical absorption spectra of transition elements in minerals reveal the change of crystal-field stabilization energy, oxidation states, site occupancy, d- or f-electron spin state, or charge-transfer process and affect radiative heat transfer, electrical conductivity, and oxidation-reduction processes in the Earth’s deep interior (Goncharov et al., 2006; Mao and Bell, 1972). Optical absorption spectra have been measured at pressures up to 80 GPa for the lower-mantle oxide magnesiowüstite. At a pressure of about 60 GPa, which corresponds to the high-spin to low-spin transition of Fe^{2+} , absorption in the mid- and near-IR spectral range was enhanced, whereas absorption in the VIS UV was reduced. These results indicate that (Mg,Fe)O with low-spin iron will exhibit lower radiative thermal conductivity than (Mg,Fe)O with high-spin iron, which is an important consideration for geodynamic models of convection and plume stabilization in the lower mantle (Goncharov et al., 2006).

2.11.4.2 IR Spectroscopy

Type II nitrogen-free diamond windows are transparent to IR radiation. Vibrational IR spectroscopy provides detailed information on bonding properties of crystals, glasses, and melts, thereby yielding a microscopic description of thermochemical properties. IR measurements also provide information on electronic excitations, including crystal-field, charge-transfer, and excitonic spectra of insulators and semiconductors, interband

and intraband transitions in metals, and novel transitions such as pressure-induced metallization of insulators. The advent of high-pressure synchrotron radiation IR spectroscopy has revolutionized such studies. IR radiation at the VUV ring of the National Synchrotron Light Source (NSLS), for example, has up to $\sim 10^4$ times the brightness of a conventional thermal (lamp) source. The significant enhancement in our ability to probe microscopic samples provided by this source makes it ideally suited to studies of materials under extreme pressures. When coupled with a Fourier transform IR (FT-IR) interferometer and special microscopes for high-pressure cells, recent work has demonstrated a gain of up to five orders of magnitude in sensitivity relative to a grating system commonly used for high-pressure IR measurements. Whereas enhanced flux can also be achieved with new IR laser techniques (e.g., optical parametric oscillators and diode lasers (Cui et al., 1995)), the very broad spectral distribution, ease of interfacing with a conventional FT-IR instrument, and the picosecond time structure provide important advantages over such techniques.

New synchrotron IR experiments have led to a series of discoveries into the nature of the Earth and planetary materials at ultrahigh pressures (Hemley et al., 1998). Study of dense hydrogen in a DAC led to the discovery of a number of unexpected phenomena, including striking intensity enhancements of vibrational modes (Hanfland et al., 1993; Hemley et al., 1994), an unusually complex phase diagram (Goncharov et al., 1995; Mao and Hemley, 1994; Mazin et al., 1997), and new classes of excitations in the solid (Soos et al., 1995). This system is exceedingly rich in physical phenomena and continues to be a crucial testing ground for theories of condensed-matter physics (Mao et al., 1994) and for planetary modeling (Hemley and Mao, 1998). The behavior of H₂O ice under pressure not only is important for planetary science but also is of broad fundamental interest. It was predicted 35 years ago (Holzapfel, 1972) that under pressure, ice should transform to a very different structure in which conventional hydrogen bonding is lost and the hydrogen atoms are symmetrically disposed between the oxygens. Synchrotron IR measurements have found that ice is indeed profoundly altered at very high pressures. At 60 GPa, synchrotron IR reflectivity measurements show that the material transforms to a new structure that has the spectroscopic signature of the symmetrical state (Goncharov et al., 1996). The new form of ice is stable to record pressure of 210 GPa. Under these conditions, ice is no longer a molecular solid but is best described as a dense ionic oxide.

2.11.4.3 Raman Spectroscopy

Raman spectroscopy is widely used for characterizing structural, vibrational, and electronic properties of minerals at high pressures (McMillan et al., 1996) and can provide fingerprinting diagnoses of high-*P-T* phases and melting. The appearance and intensity of Raman peaks follow selection rules that are governed by the symmetry of the transition, and the shift of Raman peaks indicates a change in bonding or electronic energy levels.

Developments in Raman spectroscopy technology have taken quantum leaps in the past three decades: from the scanning double-monochromator system in the 1970s, to the

subtractive-grating filter stage and dispersive spectrograph with a diode array detector in the 1980s, to the single-grating imaging spectrometers with notch filters and CCD detector in the 1990s. The Raman spectrometer has been integrated with a crossbeam (Mao et al., 1987b; Xu et al., 1986) or confocal (Gillet, 1999) microscope to achieve three-dimensional spatial resolution. New Raman spectrometers are much more sensitive and compact and thus easily coupled DACs for measurement at ultrahigh pressures and varying temperature (Goncharov and Struzhkin, 2003).

Micro-Raman (Gillet, 1999; Mao et al., 1987b) was the first technique that enabled in situ characterization of samples at high *P-T* with μm spatial resolution. With ΔE in the range of several cm^{-1} ($1 \text{ cm}^{-1} = 8 \text{ meV}$) to several thousand cm^{-1} , Raman peaks are largely due to molecular or lattice vibrations but cover some electronic and magnetic excitations also (Goncharov and Struzhkin, 2003). Micro-Raman spectroscopy has been used extensively as a structural probe for distinguishing high-pressure polymorphs of the same composition, for example, the identification of ikaite (Shahar et al., 2005) and various crystalline and amorphous phases of silica (Hemley et al., 1986) including the soft-mode transition from stishovite to the CaCl₂ structure (Kingma et al., 1995). Elastic properties can be deduced from Raman measurement of lattice phonons as demonstrated by the estimation of c_{44} modulus of h.c.p. iron from the Raman E_{2g} phonon (Merkel et al., 2000) and an intermolecular potential study based on the H₂ Raman lattice phonon (Hemley et al., 1990). Raman spectroscopy is the most definitive diagnostic tool for the identification of specific molecules or molecular species. For instance, it was used as the definitive evidence for the x-ray-induced breakdown of H₂O into H₂ and O₂ at high pressure (Mao et al., 2006b; Figure 14). The multiplicity and shift of molecular Raman peaks have also been used as diagnostic evidence for phase transitions in simple molecular compounds (Mao et al., 2002; Santoro et al., 2006; Somayazulu et al., 1996).

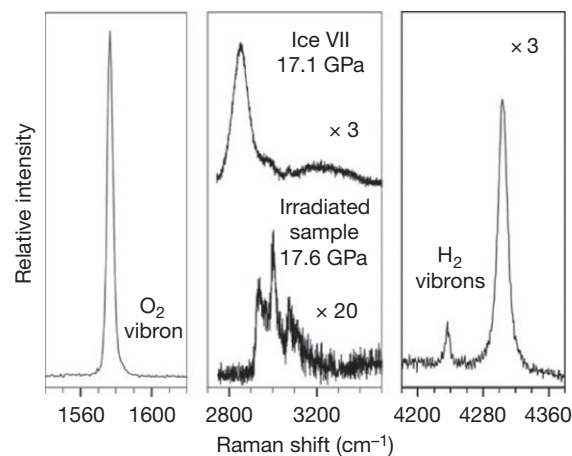


Figure 14 Raman spectra for irradiated H₂O sample at 17.6 GPa showing O₂ and H₂ vibrons, which indicates cleaving of the OH bonds and formation of O–O and H–H bonds. Raman spectra of an unirradiated ice VII sample at 17.1 GPa are shown in the second panel for comparison. Reproduced from Mao WL, Mao HK, Sturhahn W, et al. (2006) Iron-rich post-perovskite and the origin of ultralow-velocity zones. *Science* 312: 564–565.

2.11.4.4 Brillouin Spectroscopy and ISLS Spectroscopy

Much of our information on the detailed structure of the deep Earth has been derived from seismic observations in the form of wave velocities (i.e., in the laboratory, velocities of acoustic waves in a crystal can be obtained at high pressure with Brillouin spectroscopy (Bassett and Brody, 1977)), in which a laser beam is scattered by the moving acoustic waves in the sample and the Doppler shift of the laser frequency reveals the wave velocity. Unlike Raman shifts that are usually tens to thousands of wave numbers (cm^{-1}) from the elastic line, Brillouin shifts are typically less than 1 cm^{-1} . A multiple (3–6) pass Fabry–Perot interferometer is typically used for gaining the extremely high resolution and rejecting the background caused by Rayleigh scattering of the laser line. By measuring velocities of a primary (longitudinal) wave, V_p , and two secondary (shear) waves, v_s , as functions of orientation in a high-pressure single crystal, the elasticity tensor (s_{ij} or c_{ij}) can be completely characterized. Refractive indices and phase transitions at high pressure can also be investigated with Brillouin spectroscopy as by-products (Brody et al., 1981).

Brillouin spectroscopy has been used extensively for measuring elasticity tensor of major mantle minerals and glasses to lower-mantle pressures. The large database includes single-crystal forsterite (Duffy et al., 1995b; Zha et al., 1996), $(\text{Mg,Fe})_2\text{SiO}_4$ olivine (Zha et al., 1998), wadsleyite (Zha et al., 1997), hydrous ringwoodite (Wang et al., 2006) pyrope, grossular, andradite (Conrad et al., 1999), silicate perovskite (Jackson et al., 2004b, 2005c; Sinogeikin et al., 2004), calcium oxide (Speziale et al., 2006), magnesium oxide (Zha et al.,

2000), silica glass (Zha et al., 1994), silicate glass (Tkachev et al., 2005a,b), and superhard nitrides (Tkachev et al., 2003). High-pressure Brillouin spectroscopy yielded crucial information of single-crystal elasticity of hydrogen (Zha et al., 1993) and helium (Zha et al., 2004), the major components in the solar system, and provided experimental constraints to interior models of Jupiter (Duffy et al., 1994). It is a powerful tool for studying intriguing mineral physics phenomena. For instance, single-crystal elasticity of α -quartz was studied in a helium medium to 22 GPa, and the Brillouin measurements revealed a ferroelastic transition nature driven by softening of c_{44} through one of the Born stability criteria.

The extension of Brillouin system capabilities to elevated temperatures with resistive heating has enabled studies of the sound velocity of supercritical fluid hydrogen at high pressures, which has application to understanding gas giants (Matsuishi et al., 2002, 2003). Measurement of Brillouin spectra at simulated geotherm *P-T* conditions has been a long-sought-after goal for experimental geophysics but requires being able to reach significantly higher temperatures. Recently, the doughnut-absorber, double-sided, laser-heating technique has been developed for obtaining Brillouin spectra of H_2O up to 21.8 GPa and 1170 K (Figure 15; Li et al., 2006), opening many possibilities for high-*P-T* Brillouin studies (Kuwayama et al., 2005; Mao et al., 2006c; Murakami et al., 2004).

Single-crystal wave velocities have also been obtained up to 20 GPa with a related laser technique, the ISLS (Crowhurst et al., 2004). In ISLS, a laser beam is split into two beams and recombined to form a standing wave grating; a second

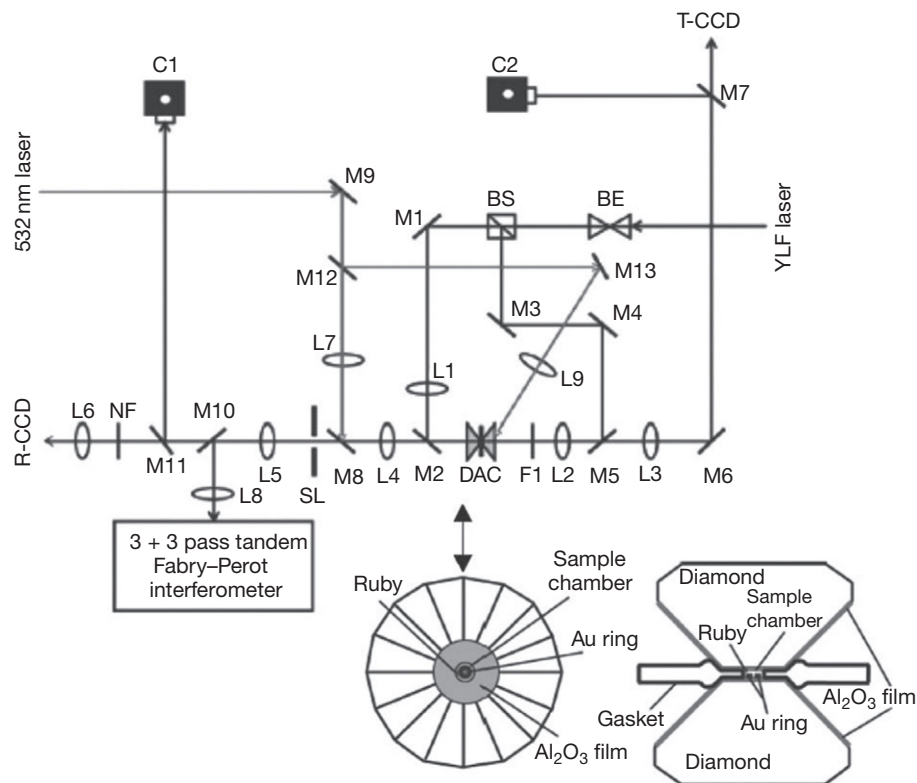


Figure 15 Laser-heating system for Brillouin and Raman scattering in DAC. Reproduced from Li F, Cui Q, He Z, et al. (2006) Brillouin scattering spectroscopy for a laser heated diamond anvil cell. *Applied Physics Letters* 88: 203507.

laser is scattered from the grating. The data are collected in the time domain, rather than the frequency domain as in the case of Brillouin scattering. In addition to acoustic velocities, high-pressure thermal diffusivity can be obtained with ISLS (Chai et al., 1996). Recent developments have combined these two techniques for simultaneous measurement in both the frequency and time domains (Crowhurst et al., 2004).

2.11.4.5 Fluorescence Spectroscopy

In fluorescence spectroscopy, electron in the sample is first excited by incident photon to an excited energy state, and then, the characteristic fluorescence photon is emitted when the electron falls back to the ground state. Energy levels in the sample are revealed as fluorescence photon energy equal to the energy difference of the two states (ΔE). Unlike Raman peaks that move with the excitation laser frequency ($\nu = \nu_{\text{laser}} - \Delta E$), fluorescence peaks appear at frequencies $\nu = \Delta E$ independent of the excitation laser frequency. Another major difference is that the Raman transition is instantaneous with $< \text{fs}$ lifetime, whereas the fluorescence spectra have a wide range of lifetimes that can range from picoseconds to milliseconds and even up to seconds.

The long-lifetime characteristics of the fluorescence peaks are often exploited for distinguishing peaks with different origins (Eggert et al., 1989).

Electronic states can be tuned continuously with pressure or change abruptly at transitions. Monitoring the frequency and lifetime of the fluorescence as a function of pressure reveals detailed changes in electronic states, providing a valuable tool for mineral physics. Minerals containing transition or rare Earth elements often emit rich fluorescence corresponding to their complicated d- and f-electron states. These minerals are valued for their wide range of luminescence, laser materials, and gemological applications. Fluorescence can also be caused by other nontransition element origins. For instance, under strain, the diamond anvils can develop intense fluorescence (Mao and Hemley, 1991).

The pressure tuning of fluorescence spectra provides a scale for calibrating the pressure itself (Barnett et al., 1973; Picard et al., 2006). Unlike Raman peaks that only broaden slightly at high temperature, the commonly used ruby fluorescence peaks become too broad to be useful above 400 °C (Sung, 1976). Fluorescence peaks originating from 4f electrons often remain sharper at high temperatures than the 3d electron Cr^{3+} fluorescence peaks of ruby, and rare Earth-doped YAG crystals can be used as a high-*P-T* calibrant substitute for ruby. For instance, Sm:YAG (Hess and Schiferl, 1992; Liu and Vohra, 1994) and other rare Earth-doped oxide garnets (Hua and Vohra, 1997; Hua et al., 1996) have been used for this purpose. The spectrometer is gated to optimize the characteristic lifetime of the fluorescence of calibrants while minimizing the thermal black-body radiations, which have an infinite lifetime.

2.11.5 x-Ray Probes

x-Rays are a versatile probe for reaching samples in the DAC and obtaining information by various diffraction and spectroscopic techniques. XRD has long been the bread-and-butter

probe for studying structure in situ at high pressure. XRD is governed by the Bragg equation:

$$\lambda = 2d \sin \theta \quad [6]$$

where λ is the x-ray wavelength, d is the crystallographic interplanar spacing, and θ is the diffraction angle. The d-spacings of different lattice planes (hkl) can be determined by angular-dispersive x-ray diffraction (ADXRD), which uses monochromatic x-radiation with a fixed λ and records the diffraction rings on two-dimensional detectors from which different θ are measured. Alternatively, d-spacings can also be determined by energy-dispersive x-ray diffraction (EDXD) using polychromatic (white) x-radiation at a fixed θ and recording diffraction peaks at different energies with a solid-state, intrinsic germanium detector, where the x-ray energy (E) is related to the wavelength by

$$E \text{ (keV)} * \lambda \text{ (\AA)} = 12.3986 \text{ (keV} * \text{\AA)} \quad [7]$$

Before 2000, most x-ray DAC experiments were conducted with XRD, except for a small number of x-ray absorption studies. Recent development at third-generation synchrotron x-ray facilities has resulted in an enormous increase in the use of XRS that is revolutionizing DAC studies.

2.11.5.1 Axial XRD

With an incident x-ray beam passing through one anvil along the DAC compression axis, impinging upon the sample, and diffraction rings exiting through the second anvil, axial XRD has been long established as the standard method for studying high-pressure crystallography, phase transitions, *P-V-T* EOS (Mao et al., 1967, 1990), lattice strain (Duffy et al., 1995a), melting (Saxena et al., 1995; Yoo et al., 1995), and pressure-induced amorphization (Hemley et al., 1988), as well as radial distribution functions of amorphous materials (Meade et al., 1992). Ultrahigh-*P-T* conditions are achieved at the expense of diminishing sample size leading to increasingly weaker XRD signals that are often overwhelmed by the background signals caused by the surrounding area that usually consists of high-*Z* materials (such as the Re gasket). Successful experiments critically depend upon the ability to focus more photons into the minute sample region, which is at the maximum *P-T*, and cutting off the 'tail' of the focused beam outside of the maximum-*P-T* region. Examples are too numerous to mention, but a few recent ones demonstrate what is possible at the current forefront of XRD DAC mineral physics research. In an in situ XRD study of alumina up to 136 GPa and 2350 K, a phase transformation was discovered at 96 GPa. Rietveld full-profile refinements demonstrated that the high-pressure phase has the Rh_2O_3 (II) (*Pbcn*) structure. This phase is structurally related to corundum, but the AlO_6 polyhedrons are highly distorted, with the interatomic bond lengths ranging from 1.690 to 1.847 Å at 113 GPa (Lin et al., 2004a).

The Earth's *D''* layer represents the lowermost 130–300 km of the silicate mantle just above the liquid outer core. In 2004, the postperovskite (ppv) silicate phase was synthesized at core-mantle boundary conditions and characterized experimentally using XRD (Murakami et al., 2004; Oganov and Ono, 2004). This discovery has generated considerable interest since ppv

may be the most abundant mineral in the D'' layer (Helmberger et al., 2005), and it may be able to explain a number of the complex seismic features of this region. It is critical to understand its crystal physics and to determine accurate values for the physical and chemical properties of this phase (Shieh et al., 2006) as they provide important input and constraints for deep-Earth models and calculations. Unlike previously known lower-mantle silicate phases, ppv can accommodate a significant amount of iron (i.e., $\text{Fe}/(\text{Fe} + \text{Mg}) > 0.6$) (Mao et al., 2005a; Figure 16). The ultimate relevance of iron-rich ppv to the Earth's D'' layer depends on the Fe–Mg partitioning between the magnesiowüstite, ferromagnesian perovskite, and ppv silicate phases in the presence of a large reservoir of liquid iron (Kobayashi et al., 2005; Murakami et al., 2005).

2.11.5.2 Radial XRD

Contrary to the hydrostatic condition that is often viewed as the most desirable, the nonhydrostatic stress in samples compressed in solid medium was generally considered as a nuisance that degrades the experiments. The study of iron in a Be gasket (Mao et al., 1998b) and wüstite in an amorphous boron gasket (Mao et al., 1996) with radial XRD demonstrated that the nonhydrostatic stress, if properly characterized, contained a wealth

of elastic and rheological information far more than the information from hydrostatic compression alone and that hydrostatic and nonhydrostatic measurements are complementary.

Elasticity information can be obtained from probing stress–strain relations in a uniaxially compressed sample. Superimposing a uniaxial compression onto a polycrystalline aggregate already under a confining pressure (*P*) produces a deviatoric strain (ϵ_ψ) that is a function of the angle (ψ) between the direction of the strain and the compression axis:

$$\epsilon_\psi(hkl) = \frac{d_\psi(hkl) - d_p(hkl)}{d_p(hkl)} = (1 - 3\cos^2\psi) \cdot Q(hkl) \quad [8]$$

where $d_\psi(hkl)$ is the lattice spacing measured at ψ and $d_p(hkl)$ is the lattice spacing under hydrostatic pressure. The slope $Q(hkl)$ is a constant for elastically isotropic materials but varies with hkl for elastically anisotropic materials and is an excellent quantitative measure of the direction and degree of elasticity anisotropy. Singh et al. (1998a) further developed the formalism for different crystal systems for calculating the full elastic tensor (c_{ij} 's) and velocity anisotropy based on $Q(hkl)$ and additional information from the axial compressibilities (χ_a and χ_b) and the aggregate shear modulus (*G*), which come from the EOS and NRIXS data, respectively.

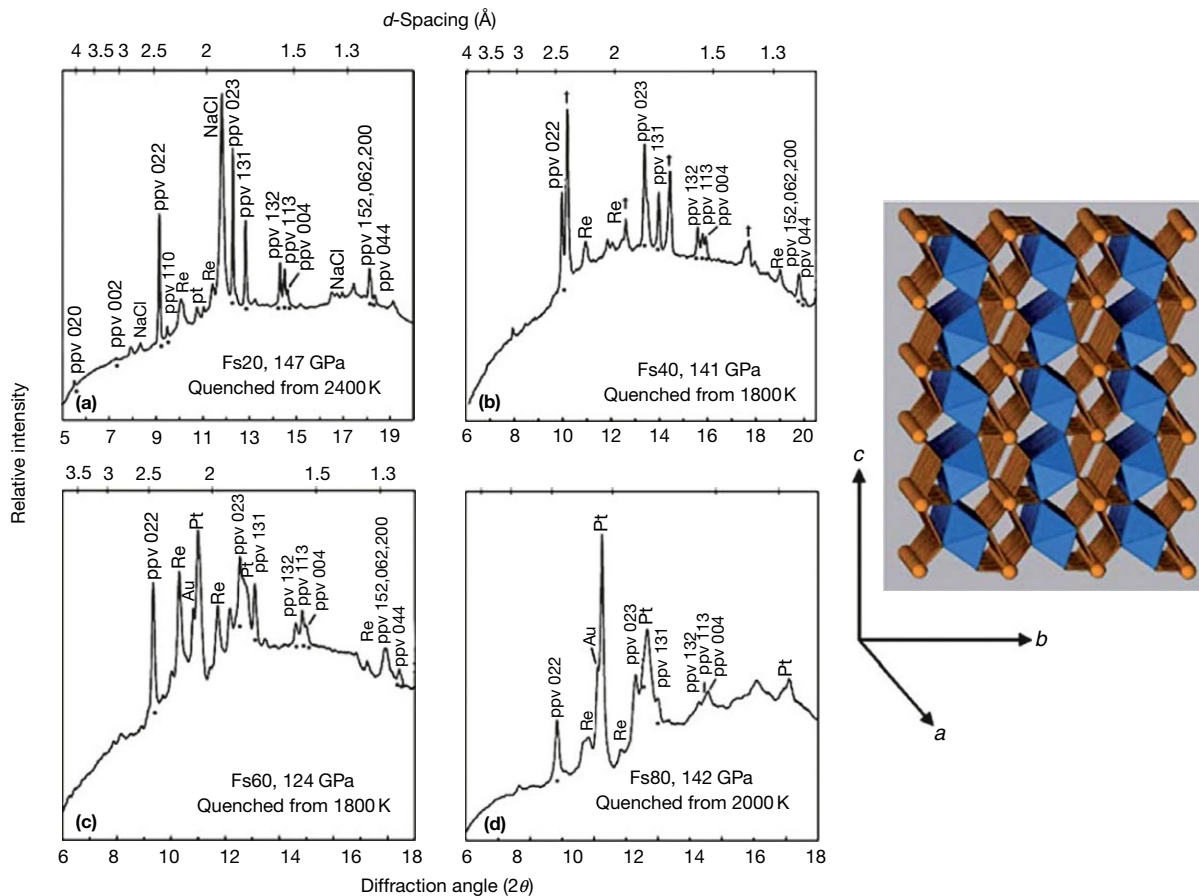


Figure 16 x-Ray diffraction patterns for (a) Fs20 ($\text{Mg}_{0.8}\text{Fe}_{0.2}\text{SiO}_3$) at 147 GPa ($\lambda = 0.3888 \text{ \AA}$); (b) Fs40 at 141 GPa ($\lambda = 0.4233 \text{ \AA}$); (c) Fs60 at 124 GPa ($\lambda = 0.4008 \text{ \AA}$); and (d) Fs80 at 142 GPa ($\lambda = 0.4057 \text{ \AA}$). ppv peaks are additionally marked with *. Re oxide peaks are marked with †. The crystal structure of ppv is shown on the right where silicon octahedral are shown in blue and iron and magnesium cations are shown in orange.

To measure strain as a function of ψ , Kinsland and Bassett (1976) developed a DAC that had a large side opening that could access the full range of ψ directing x-rays perpendicular to the diamond axis (radial direction) onto the sample. Mao et al. (1998b) made modifications and developed a panoramic DAC that extended radial XRD capabilities to megabar pressures by the use of an x-ray transparent Be gasket and analyzed the elasticity of h.c.p. iron to 220 GPa using the Singh formalism. This technique has also been used successfully for studying the elasticity and strength of mantle silicates and oxides below 100 GPa (Kavner, 2003; Shieh et al., 2002, 2004).

There have been concerns surrounding assumptions related with inverting the polycrystalline XRD data to calculate the single-crystal elastic tensor. A more recent ambient temperature radial XRD study to lower pressure (30 GPa) of the single-crystal elasticity of h.c.p. iron demonstrated progress in constraining uncertainties in the radial XRD technique (Merkel et al., 2005). Besides improvements that come with using large-area detectors, which enable precise measurements of the variation of d-spacing with orientation and texture analysis, the inversion of elastic moduli was more sophisticated, including effects of lattice-preferred orientation in the analysis (Matthies et al., 2001) and using the constraint of the c_{44} elastic modulus measured using Raman spectroscopy (Merkel et al., 2000). For this lower-pressure study, the shape of the anisotropy that was obtained was the same as the previous work by Mao et al. (1998b) (i.e., in the body diagonal between the *a* and *c*-axes), but the overall magnitude was reduced.

In a very recent study of an analog material h.c.p. cobalt, Merkel et al. (2006b) further demonstrated that calculations need to include the orientation dependence of differential stress resulting from plastic deformation. Studies using inelastic x-ray scattering spectroscopy (see Section 2.11.5.9) on single-crystal h.c.p. cobalt indicate that the fast direction is in the *c*-axis (Antonangeli et al., 2005), which matches well with theory, whereas radial XRD results on polycrystalline h.c.p. cobalt show a fast body diagonal. The error from radial XRD comes from the large-shear strength anisotropy in this system and may be a significant problem for using radial XRD studies on polycrystalline h.c.p. iron to interpret the source of inner-core anisotropy.

The shear strength, elastic moduli, elastic anisotropy, and deformation mechanisms of the two main end-member phases of the lower-mantle MgO and (Mg_{0.9}Fe_{0.1})SiO₃-perovskite have been studied using radial XRD up to 47 and 32 GPa at ambient temperature (Merkel et al., 2002, 2003). It was demonstrated that the elastic moduli of MgO obtained with the radial diffraction method are in agreement with the more precise Brillouin spectroscopy studies. The uniaxial stress component in the polycrystalline MgO sample is found to increase rapidly to 8.5 GPa at a pressure of 10 GPa in all experiments. The uniaxial stress supported by the perovskite aggregate is found to increase continuously with pressure up to 10.9 GPa at 32 GPa. A comparison between the experimental textures and results from polycrystal plasticity gives information regarding the preferred orientation and deformation mechanism of MgO under very high confining pressure at room temperature. Under axial compression, a strong cubic texture developed in MgO could be the source of seismic anisotropy. On the other hand, the measurements displayed no development of

significant lattice-preferred orientations in the perovskite sample, indicating that deformation by dislocation glide is not the dominant deformation mechanism under these conditions. Assuming that the underlying cause for seismic anisotropy in the deep Earth is elastic anisotropy combined with lattice-preferred orientation, these results indicate that silicate perovskite deformed under the conditions of this experiment would not be the source of seismic anisotropy.

The radial XRD technique has more recently been implemented with CCD detectors, allowing collection of two-dimensional (δ - and d -spacing) diffraction with a monochromatic x-ray beam. The sample is compressed in a wide-angle panoramic DAC and heated with the double-sided laser-heating technique. A study that monitored the development of lattice-preferred orientation in a radial XRD experiment on MgGeO₃ ppv to above 100 GPa found that the (100) and (110) slip systems dominate the plastic deformation in this germinate analog. The results provide a new mechanism for development of D'' seismic anisotropy (Merkel et al., 2006a).

Both elasticity and rheology can be highly temperature-dependent. The next frontier to be explored is radial XRD study in situ at high-*P-T* conditions analogous to those in the Earth's deep interior. A study of b.c.c. and h.c.p. iron with angle-dispersive radial XRD measurements under nonhydrostatic conditions up to 30 GPa and 1000 K in laser-heated DAC found that b.c.c. iron developed preferred orientation compatible with observations under ambient conditions. The preferred orientation of the b.c.c. phase is inherited by the h.c.p. phase in accordance with the Burgers orientation relationship, consistent with a martensitic nature of the phase transition. A comparison between the observed texture in h.c.p. iron with results from polycrystal plasticity modeling suggests that the predominant deformation mechanisms are basal slip and prismatic slip presumably associated with minor mechanical twinning rather than the slip systems that were proposed based on analogy to Cr-Ni alloys (Mao et al., 1998b; Merkel et al., 2004, 2005).

2.11.5.3 Single-Crystal XRD

Single-crystal XRD experiments are unique and important sources of structural information crucial for understanding the microscopic mechanisms of high-pressure phenomena. High-pressure single-crystal XRD burgeoned with the invention of 'Merrill-Bassett' DAC (Merrill and Bassett, 1974) that provided a simple, robust hardware and the development of data collection and processing software by Larry Finger (Hazen and Finger, 1982). A large quantity of high-precision, high-pressure, crystallography data has been collected on single-crystal mineral samples, including troilite (King and Prewitt, 1978), coesite (Levien and Prewitt, 1981), albite (Benusa et al., 2005), wüstite (Jacobsen et al., 2005), MgSiO₃-perovskite (Ross and Hazen, 1989; Vanpeteghem et al., 2006), sillimanite, andalusite (Burt et al., 2006), bernalite (Welch et al., 2005), and mica (Smyth et al., 2000). Subtle, displacive, high-pressure, phase transitions were discovered in single-crystal pyroxenes (Arlt et al., 2000; Jackson et al., 2004a). New rules governing the compression of ionic radii (Shannon and Prewitt, 1970) and tilting of polyhedrons were proposed (Angel et al., 2005; Hazen and Finger, 1982). Single-crystal

data are used to resolve some very difficult crystallographic problems, for example, the recent solution of the O8 chain structure (Lundegaard et al., 2006).

Compared to other ultrahigh-pressure DAC methods, which typically cover pressure ranges as high as 300 GPa, the pressure range for single-crystal XRD lags far behind. Reports of single-crystal XRD structural analysis are limited to 30 GPa, above which there are only a handful of studies that only provide determination of the orientation matrix and unit cell parameters (e.g., hydrogen with the simple h.c.p. structure to 119 GPa (Loubeyre et al., 1996)) and not full structure refinement. A high-pressure workshop was organized to address the problem of single-crystal XRD structure refinement at megabar pressures (Dera et al., 2005), and many different approaches were proposed. The problem will be solvable with sufficient effort. A solution to the problem is emerging with the recent development of the panoramic DAC (Mao et al., 2001), which allows nearly full access around the equatorial plane, as well as both poles of the DAC, and the micro-single-crystal XRD method (Ice et al., 2005; Larson et al., 2002; Tamura et al., 2002), which combines microfocusing, EDXD, and ADXD for single-crystal XRD with sub-mm resolution (Figure 17).

2.11.5.4 x-Ray Absorption Spectroscopy

In x-ray absorption spectroscopy (XAS), the incident x-ray is absorbed when its energy exceeds the excitation energy of deep-core electrons of a specific element in the sample, causing an edge-like absorption spectrum. The x-ray absorption near-edge structure (XANES) within tens of eV to the edge provides information on the symmetry-projected conduction band DOS that is related to the electronic properties including oxidation state, crystal-field splitting, and magnetic spin pairing (Ablett et al., 2003; Jackson et al., 1993). The extended x-ray absorption fine structure (EXAFS) to several hundreds of eV above the edge provides local structure information that is particularly valuable for amorphous materials or in low concentrations

that XRD method is inapplicable (Anderson et al., 2002; Bassett et al., 2000; Mayanovic et al., 2003). These powerful, element-specific probes reveal the electronic and structural changes taking place at high pressure (Itie et al., 1992).

XAS was one of the first XRS techniques applied to high-pressure synchrotron radiation research but was previously limited to higher energies due to absorption by the diamond anvils. In addition, the Laue diffraction of single-crystal diamonds causes sharp absorption peaks that are detrimental to EXAFS spectroscopy. To greatly reduce the amount of diamond in the beam path, holes are drilled in diamond anvils in the newly developed Bassett-type hydrothermal DAC for studying L-edge of rare Earth ions and K-edge of transition element ions in supercritical aqueous solutions at moderate-*P*-*T* conditions (Figure 18; Anderson et al., 2002). The results reveal structural relaxations of ligand-anion complex at increasing *P*-*T* in mineralizing hydrothermal fluid.

Alternative beam paths through high-strength beryllium and boron gaskets are used in the new panoramic DAC at higher pressures (Mao et al., 2001). Both techniques extend XAS down to 4 keV, which covers the K-edges of first-row transition elements and the L-edges of rare Earth elements. Specific electronic, magnetic, and optical properties of these elements are crucial for a wide range of applications in materials sciences and technology.

2.11.5.5 x-Ray Emission Spectroscopy

In x-ray emission spectroscopy (XES), core electrons in the sample are excited by x-rays and subsequently produce fluorescence photons. The energies of the fluorescence photons are analyzed with sub-eV energy resolution of the emission spectral line shape to provide valuable information on the filled electronic states of the sample. With the panoramic DAC that extends the low end of the high-pressure energy window down to 4 keV, deep-core electron elements heavier than calcium can now be studied at high pressure by a suitable choice of analyzer

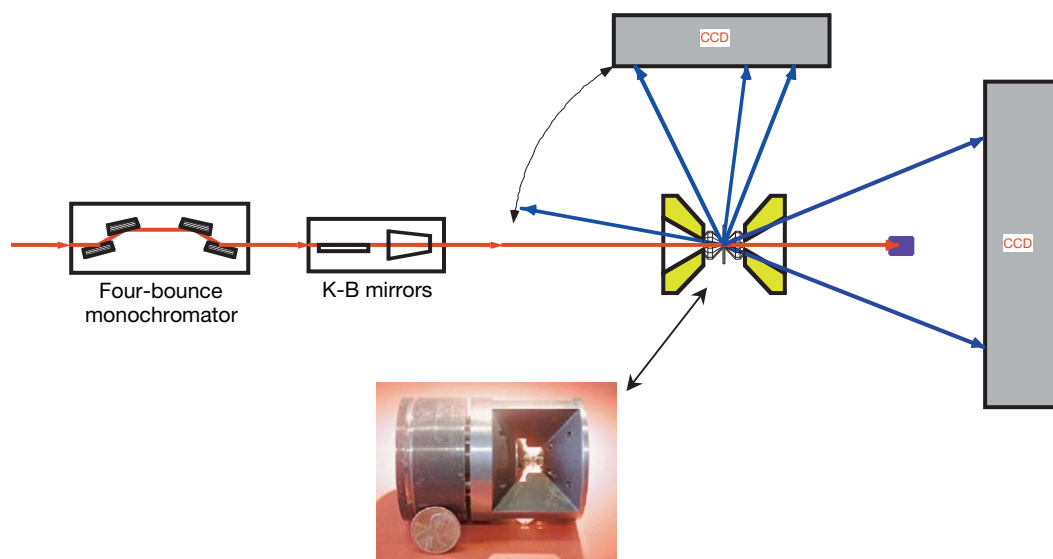


Figure 17 Integrated high-pressure micro-single-crystal XRD and XRS with panoramic DAC for both forward and 90° Laue diffraction and spectroscopy.

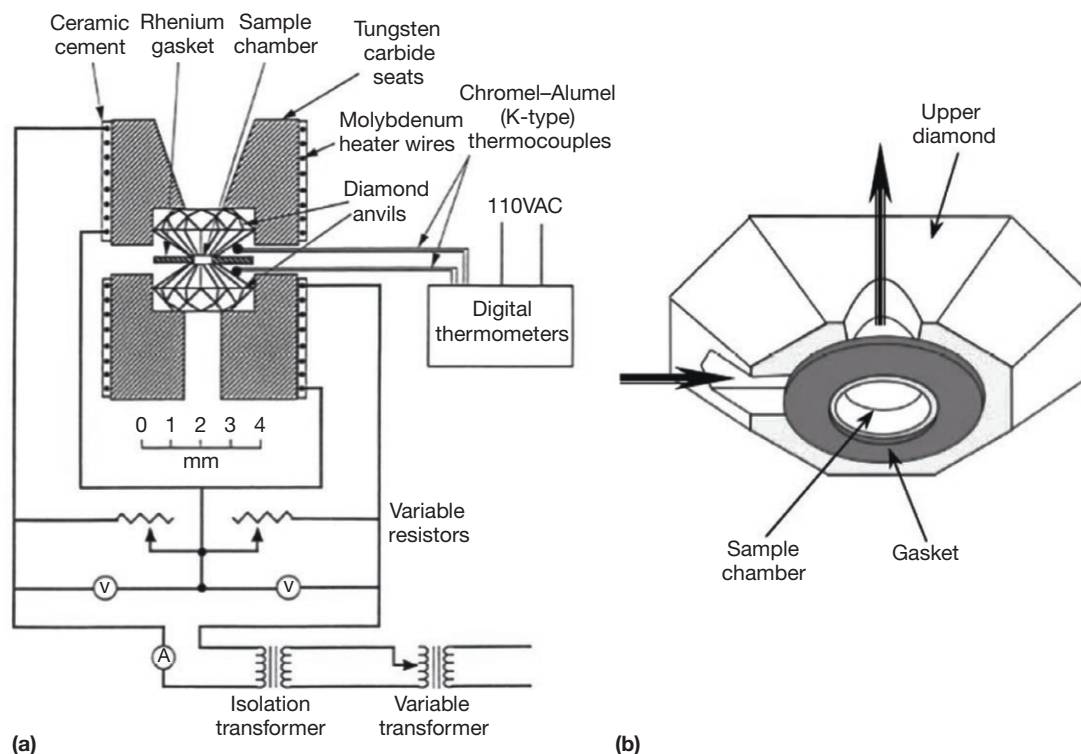


Figure 18 (a) A schematic diagram of a Bassett-type hydrothermal diamond-anvil cell (HDAC). (b) The schematic diagram of the upper diamond of the modified HDAC showing the entrance and exit grooves for the incident and fluorescence x-rays, respectively. The laser-drilled sample chamber is located in the center of the upper diamond-anvil face above the hole in the gasket. Reproduced from Anderson AJ, Jayanetti S, Mayanovic RA, Bassett WA, and Chou IM (2002) X-ray spectroscopic investigations of fluids in the hydrothermal diamond anvil cell: The hydration structure of aqueous La^{3+} up to 300 °C and 1600 bars. *American Mineralogist* 87: 262–268.

crystals. Transition-element ions, with their variable valence and magnetic states, control major geochemical processes and geophysical behavior, such as oxidation and reduction, chemical differentiation, elasticity, geomagnetism, conductivity, and radiative heat transfer. Magnetic collapse in transition metal monoxides has been predicted from first-principles computations at the pressures of the lower mantle and core (Cohen et al., 1997). XES provides a unique probe for the diagnosis of pressure-induced magnetic spin collapse in transition elements. The ultrahigh pressures in the lower mantle and core squeeze atoms and electrons so closely together that they interact differently than under normal conditions, even forcing electrons to pair.

In high-pressure XES experiments, the incident beam energy is fixed, the emission x-radiation can be collected at any direction, and high-resolution emission spectra are obtained by a synchronized θ - 2θ scan of the analyzer and the detector. The excitation x-ray source only needs to have higher energy than that of the fluorescent photons; energy bandwidth (resolution) of the x-ray source is inconsequential. In principle, white (a broad, smooth continuum of energy), pink (an unfiltered undulator beam with energy band path of hundreds eV), and monochromatic (a narrow, eV band path of photons) x-rays can all be used as the source. In practice, if sufficient intensity is available, the monochromatic source is preferred because white and pink x-radiations often cause higher backgrounds and damage the diamond anvils.

The first high-pressure XES study was conducted by collecting the iron K_{β} emission in troilite (FeS) using the white x-ray source, the NSLS, and a high-spin to low-spin transition at 4 GPa coinciding with the FeS I–II structural transition was successfully observed (Rueff et al., 1999). Subsequently with higher source intensity, this technique has been applied with pink source and monochromatic sources at the European Synchrotron Radiation Facility and the Advanced Photon Source for studies of high-spin to low-spin transitions in key mantle and core materials and has been extended to ultrahigh pressures above 100 GPa (Badro et al., 1999, 2002, 2003, 2004; Li et al., 2004; Lin et al., 2005a). The results like the reported transitions of iron in ferromagnesian silicate perovskite, the most abundant mineral in the Earth from a high-spin to an intermediate-spin and low-spin state (Badro et al., 2004; Li et al., 2004), and electronic transitions in magnesiowüstite, the second most abundant mineral from a high-spin to a low-spin state (Badro et al., 2003; Lin et al., 2005a), have profound implications on the properties of the lower mantle and place important constraints on models of the deep mantles and cores of terrestrial planets.

2.11.5.6 Inelastic x-Ray Scattering: Near-Edge Spectroscopy

Near core-electron absorption edge features measured by soft x-ray absorption (XANES) or electron energy loss spectroscopy reveal rich information about the nature of chemical bonding.

Such information is particularly pronounced and important for light elements but has been inaccessible for high-pressure studies as the pressure vessel completely blocks the soft x-ray and electron beams. This problem has recently been overcome by applying the x-ray inelastic near-edge spectroscopy (XINES) technique to high pressure. In high-pressure XINES, the high-energy incident x-ray penetrates the pressure vessel and reaches the sample. The scattered photon loses a portion of energy corresponding to the K-edge of the low-*Z* sample but can still exit the vessel to be registered on the analyzer-detector system (Figure 3). Inelastic K-edge scattering spectra of second-row elements from Li (56 eV) to O (543 eV) at high pressures have been successfully observed at high pressures. This opened a vast, new field of near K-edge spectroscopy of the second-row elements.

In XINES experiments, single-crystal analyzers collect scattered x-radiation and focus it to the detector in a nearly back-scattering geometry, thus fixing the energy at the elastic line. The incident x-ray energy is scanned relative to the elastic line to determine the inelastic (Raman) shift. XINES features are relatively insensitive to *q*, and thus, the 2θ angle is set at an angle to optimize the intensity, and multiple analyzers can be used to increase the counting rate without concern for their differences in *q*. XINES studies of bonding changes in graphite (Mao et al., 2003a; Figure 19), hexagonal boron nitride (Meng et al., 2004), and H₂O (Cai et al., 2005; Mao et al., 2006b) demonstrate the great promise of this technique and can be easily extended to studies of bonding changes in Earth materials. For example, a more recent study of the near K-edge structure of boron and oxygen in B₂O₃ glass to 22.5 GPa revealed pressure-induced coordination changes that have clear relevance for understanding the bonding in melts and glass in the deep Earth (Lee et al., 2005).

2.11.5.7 Resonance x-Ray Inelastic Spectroscopy

In resonant inelastic x-ray scattering (RIXS) experiments, both the incident and scattered x-ray energies need to be scanned. The incident x-ray energy is scanned across the core absorption, similar to the procedures for XAS. For each monochromatic incident x-ray energy, fluorescence spectra are collected by scanning analyzers, similar to the procedures of XES spectroscopy. There have been a growing number of RIXS studies of core excitations (Kotani and Shin, 2001) where the final states of the inelastic scattering process in these studies are localized shallow-core excitations. These shallow-core excitations are the same excitations routinely probed by soft XAS and are rich in multiplet structures for these highly correlated electronic systems. In fact, the high-energy-scale parameters of the highly correlated systems are routinely derived from fitting these spectra with model calculations. For magnetic samples, excitation with circularly polarized x-rays can also provide information on spin-resolved electronic structure, for example, the L₃ edge of Gd (DeGroot et al., 1997; Krisch et al., 1996).

One can obtain selected information connected directly with a specific intermediate state to which the incident photon energy is tuned. RIXS studies of transition metal and rare Earth systems give us important information on the electronic states, such as the intra-atomic multiplet coupling, electron correlation, and interatomic hybridization. Unusual phase transitions

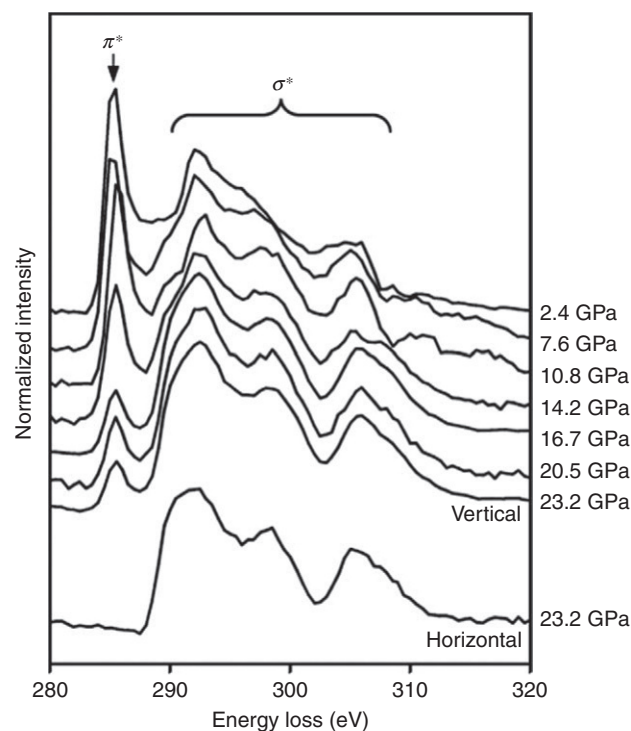


Figure 19 High-pressure IXS spectra for graphite in horizontal and vertical directions plotted as normalized scattered intensity versus energy loss (incident energy-analyzer energy). The scattered intensity is normalized to the incoming intensity. The lower-energy peak, labeled π , corresponds to $1s - \pi^*$ transitions, and the higher-energy portion, labeled σ , corresponds to $1s - \sigma^*$ transitions. The bottom spectra, taken in the horizontal direction, probe bonds in the π -plane and do not show any w -bonding before and after the high-pressure transition. The top seven spectra, taken in the vertical direction, probe the c -plane. After the transition, the σ bonds increase at the expense of the π bonds. Reproduced from Mao WL, Mao HK, Eng P, et al. (2003) Bonding changes in compressed superhard graphite. *Science* 302: 425–427.

driven by electron correlation effects occur in many transition metals and transition metal compounds at high pressures, some accompanied with large volume collapses (e.g., 5–17% in rare Earth metals and 10–15% in magnetic 3d transition metal oxides). However, the exact nature of these transitions is not well understood, including the relationships between the crystal and electronic structures and the role of magnetic moment and order. A RIXS and XES study of Gd metal to 113 GPa suggests Kondo-like aspects in the delocalization of 4f electrons (Maddox et al., 2006). Analysis of the RIXS data reveals a prolonged and continuous delocalization with volume throughout the entire pressure range, so that the volume-collapse transition at 59 GPa is only part of the phenomenon.

Since both incident and scattered photons are hard x-rays that are capable of entering and exiting the DAC, RIXS enable high-pressure in situ spectroscopic studies of rich shallow levels, which were previously restricted to soft x-ray, vacuum environment. Multiple electronic levels in transition metal and rare Earth ions (Hill et al., 1998; Kao et al., 1996), complexes, and clusters in minerals or solutions can be investigated in detail in DAC. For instance, the central question about the

redox conditions (Frost et al., 2004; McCammon, 2005) of deep-mantle geochemistry relies on experimental determination of $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio of minerals synthesized and quenched from high-*P-T* conditions and analyzed in vacuum with iron L2,3-edge ELNES spectroscope (Garvie et al., 2004; Sinmyo et al., 2006; van Aken and Liebscher, 2002). Caliebe et al. (1998) demonstrated that for hematite, the 1s2p RIXS process can be exploited to obtain spectroscopic information similar to that obtained in L2,3 absorption spectroscopy, thus opening the possibility of direct, in situ study of redox at ultrahigh pressure and temperature.

2.11.5.8 Nuclear Resonant XRS

Important dynamic, thermodynamic, and elastic information on a material, including vibrational kinetic energy, zero-point vibrational energy, vibrational entropy, vibrational heat capacity, the Debye temperature, the Grüneisen parameter, thermal expansivity, longitudinal velocity, shear velocities, bulk modulus, and shear modulus, can be derived from knowledge of the phonon DOS. Studies of the phonon DOS are greatly simplified if the element involved has an isotope that exhibits a nuclear resonant Mössbauer effect. In nuclear resonant XRS, an in-line high-resolution monochromator is used to narrow down the photon energy to meV resolution and fine-tune the monochromatic x-ray near the exceedingly narrow nuclear resonant (elastic) line. Avalanche photodiodes (APDs) are used to collect only the signal from nuclear resonance absorption and reject nonresonantly scattered radiation. The APD directly downstream of the sample collects nuclear resonant forward scattering spectra, which can provide a precise determination of the hyperfine interaction parameter and Lamb-Mössbauer factor (Jackson et al., 2005b). The APDs surrounding the sample radially collect the NRIXS signal, which is a result of creation (Stokes) or annihilation (anti-Stokes) of phonons as the incident x-ray beam is scanned over a small range (approximately ± 100 meV) around the resonant energy. This phonon excitation spectrum can then be used to determine and calculate phonon DOS (Sturhahn et al., 1995). Although NRIXS measures the phonon DOS rather than the dispersion curve, the DOS is still rich in vibrational and dynamic information. The initial slope gives V_D , which is related to V_P and V_S by

$$\frac{3}{V_D^3} = \frac{1}{V_P^3} + \frac{2}{V_S^3} \quad [9]$$

which is related to the bulk modulus (K) and density (ρ) from XRD data by

$$V_\phi^2 = V_P^2 - (4/3)V_S^2 = K/\rho \quad [10]$$

These two equations can be used to calculate V_P and V_S . It should be noted that unlike the bulk sound speed (V_ϕ), which is more heavily dependent on V_P , V_D is more heavily dependent on V_S , so NRIXS data are particularly useful for constraining the shear properties. The integration of the whole DOS provides values for key thermodynamic properties necessary for interpreting seismological observations. Theory can be used to deconvolute the dispersion curve from the DOS.

NRIXS has been developed for the Mössbauer isotope ^{57}Fe and can be used to study samples with a minor amount of iron (Hu et al., 2003). After demonstration of DOS measurements on b.c.c. iron at ambient conditions (Lübbbers et al., 2000), NRIXS measurements have been extended to high pressure to obtain the phonon DOS of h.c.p. iron up to 153 GPa (Mao et al., 2001) and iron-related partial phonon DOS for iron alloys (Lin et al., 2003c, 2004c; Mao et al., 2004; Figure 20) and have attracted particular attention among physicists and geophysicists because iron is an archetypal transition element and is a dominant component in the cores of the Earth and other terrestrial planets (Mars, Venus, and Mercury). Using this method also carries the assumption that the sample contains a single, ^{57}Fe -bearing phase in which iron is evenly distributed that needs to be verified using XRD and microscopic techniques on quenched samples. Separation of iron into different phases would skew the V_D toward the velocity of the slower phase and give a misleading result.

More recently, the sound velocities of h.c.p. iron were determined at high *P-T* by NRIXS in a laser-heated DAC at pressures up to 73 GPa and at temperatures up to 1700 K (Lin et al., 2005b). The compressional-wave velocities and shear-wave velocities of h.c.p. iron decreased significantly with increasing temperature and thus cannot be fit to a linear relation, Birch's law, which has guided geophysicists in making correlations of seismic (sound) velocity and density for the past half-century. This result means that there are more light elements in the Earth's core than have been inferred from a linear extrapolation of data collected at ambient temperature.

Experiments simulating the high-*P-T* conditions of the core-mantle boundary observed that a large amount of iron incorporated into the ppv silicate phase can significantly change its properties relative to the pure Mg end-member (Mao et al., 2005a). The determined aggregate compressional- and shear-wave velocities of this iron-rich silicate at high pressure show that a silicate with up to 40% iron end-member can match many of the seismic features observed in ultralow-velocity zones above the core-mantle boundary. Mantle dynamics may lead to accumulation of an iron-rich silicate reaction veneer between the iron-poor lower mantle and the iron-rich outer core into ultralow-velocity patches observable by seismology (Mao et al., 2006c).

NRIXS is a very promising technique and is currently the only experimental method for constraining shear properties, but there are limitations. The NRIXS process is very inefficient. To obtain a spectra with reasonable counting statistics at an optimized third-generation synchrotron source requires a combination of long counting times (often on the order of hours), maximized sample thickness, and compositions with higher Mössbauer isotope content. This becomes increasingly difficult as researchers try to conduct experiments at higher pressures (which reduces sample size), high temperatures (which limits counting time since the sample must be stably heated over the counting interval and sample thickness since thermal insulating layers must be added), and mantle compositions (which have minor amounts of iron in their compositions). Future improvements with this technique include upgrades at the synchrotron beamline (e.g., increasing flux by adding undulators, improving focus, increasing detector efficiency, etc.), modifications in the DAC design (to allow additional

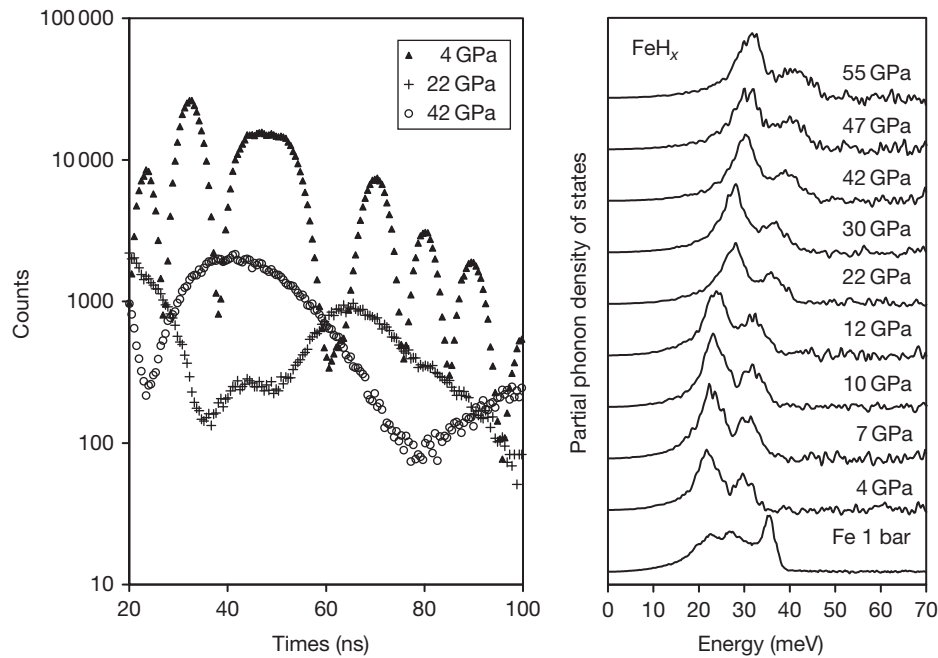


Figure 20 Left, NRFS spectra for FeH_x . Data below 22 GPa show fast oscillations diagnostic of a magnetic sample. At 22 GPa, the magnetic field becomes very small and above 22 GPa, it is negligible. Right, NRIXS spectra showing the partial phonon density of states for FeH_x at high pressure. For comparison, the density of states of pure iron at ambient pressure is shown. Reproduced from Mao WL, Struhahn W, Heinz DL, Mao HK, Shu J, and Hemley RJ (2004) Nuclear resonant X-ray scattering of iron hydride at high pressure. *Geophysical Research Letters* 31: L15618. <http://dx.doi.org/10.1029/2004GL020541>.

increased access to detectors), and use of superhard gasket inserts to increase sample thickness (Section 2.11.2.2).

2.11.5.9 Nonresonant Phonon Inelastic x-Ray Scattering

Detailed study of phonon dynamics in highly compressed materials is necessary for understanding vibrational thermodynamic properties, elasticity, and phase transition mechanisms but until very recently has eluded high-pressure experimental investigation. Nonresonant phonon inelastic x-ray scattering (PIXS) is a powerful method that holds great promise for studying phonon dynamics of Earth materials at high pressure, but this technique is still beset with many challenges. For studying phonons, the energy transfers involved are in the meV range (six orders of magnitude smaller than the incident x-rays), which makes the detection of the energy shifts due to phonon creation and annihilation challenging (Burkel, 2000). Also, the double differential scattering cross section of PIXS is very small, making such an experiment very demanding even with the brilliance of third-generation synchrotron undulator sources. In addition, there are limitations in sample size and the requirement of navigating the full beam through the high-pressure vessel and separating the very weak sample signal from the strong background signal of the vessel.

Ideally, one would want to measure the full phonon dispersion curve, which contains all the elasticity information and vibrational thermodynamic properties. Unlike optical techniques that are limited to phonons at or very near the zone center, the advantage for IXS phonon studies is access to the full range of momentum transfers (q), allowing measurement of the full dispersion curve. Single-crystal PIXS can map out the

entire phonon dispersion curve (Schwoerer-Böhning and Macrander, 1998). Single-crystal PIXS studies are potentially providing the same amount of information as inelastic neutron scattering (Klotz and Braden, 2000) and have recently been expanded to high pressures (Antonangeli et al., 2005; Farber et al., 2006; Ocelli et al., 2001; Ruf et al., 2001).

It has been established that the Earth's inner core exhibits elastic anisotropy with compressional waves traveling approximately 3% faster in the radial versus equatorial directions (e.g., Morelli et al., 1986; Song and Richards, 1996; Tromp, 2001), which makes understanding the elasticity of iron at inner-core conditions critical for interpreting seismic observations. Currently, static measurements have not reached inner-core P - T , so one role of experimental results is the verification of theory, which is not limited in P - T range but has produced conflicting results for the elastic anisotropy of h.c.p. iron. High-pressure PIXS studies of polycrystalline iron (since large single-crystal samples of h.c.p. iron cannot be synthesized), which measure phonon excitations corresponding to scattering of the incident x-ray photons by longitudinal acoustic phonons, have been conducted to over 100 GPa (Antonangeli et al., 2004; Fiquet et al., 2001). These studies show great promise for studying elasticity, but they were conducted axially, which limits the access of the uniaxial strain field that develops in the DAC, and a preferred orientation of the sample is assumed rather than measured. Also, thus far, V_s has never been detected in IXSS studies of h.c.p. iron, and the measurement is limited to V_p . While the study by Antonangeli et al. (2004) shows variations in V_p for 50° and 90° relative to the DAC compression axis, multiple points over the full angular range are needed to constrain the shape of the velocity

anisotropy. A future advance would be the use of an x-ray transparent gasket that would allow access to the full angular range and determination of the preferred orientation of the sample.

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2.12 Theory and Practice: Techniques for Measuring High-P–T Elasticity

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2.12.1 Introduction

Since the early part of the twentieth century, it has been recognized that elastic modulus measurements are essential for understanding the composition and structure of the Earth, especially the deep portions of the Earth that are not sampled directly. This connection between elasticity and the properties of the deep Earth arises naturally, because the field of seismology gives us the acoustic wave velocities throughout the Earth, with ever-increasing detail, whereas the acoustic velocities of minerals are in turn determined by their elastic moduli. Therefore, if we are to utilize the rich source of information on velocity variations in the Earth's interior to infer basic properties such as composition and temperature, this requires knowledge of the elastic properties of Earth materials. At perhaps an even more fundamental level, the bulk modulus $K_T = \rho(\partial P / \partial \rho)_T$ (the incompressibility) gives the variation with density with pressure (or depth). Thus, Adams and Williamson (1923) used the few available measurements of elastic wave velocities and the bulk moduli of some rocks and iron metal to determine a density and pressure distribution in the Earth. Much later, Birch (1952) used a broader database on the elastic properties of materials and more modern seismic velocity profiles to make improved inferences about the composition and temperature at depth. These classic studies illustrate the long-standing interest in the experimental determination of the elastic properties of Earth materials.

In principle, the isothermal bulk modulus is readily measured by imposing a known pressure on a sample and

measuring the resulting change in volume or density. These measurements can be done in a variety of ways, some of which will be described in the following sections. One of the challenges in geophysical studies is that many minerals are relatively incompressible, especially high-pressure phases. Moreover, to exploit the information provided by seismological studies, it is necessary to consider the adiabatic elastic properties that govern the propagation of longitudinal and transverse elastic waves in a material, v_P and v_S , respectively. For an isotropic material, the appropriate relations are

$$v_P = \sqrt{\frac{K_S + (4/3)\mu}{\rho}}, \quad v_S = \sqrt{\frac{\mu}{\rho}} \quad [1]$$

$$K_S = \rho \left(v_P^2 - \frac{4}{3} v_S^2 \right), \quad \mu = \rho v_S^2 \quad [2]$$

where ρ is the density, K_S is the adiabatic bulk modulus, and μ is the (adiabatic) shear modulus. The determination of these quantities for Earth materials, using both experimental and theoretical approaches, continues to be one of the main thrusts in experimental geophysics. Clearly, measurements at elevated pressures and temperatures are important for applications to the Earth's interior.

We may separate measurements of elastic properties (both elastic moduli and elastic wave velocities) into two broad classes: those on polycrystalline materials and single-crystal measurements. Polycrystalline materials include natural rocks or other polyphase assemblages and aggregates of a single

phase. If the samples have randomly oriented grains, then the aggregate velocities and moduli of eqn [1] are obtained directly. Care must be taken to minimize or eliminate the effects of any cracks, pores, and preferred orientations of grains (fabric). The effects of such imperfections or microstructures are sometimes difficult to identify or account for. An alternative approach is to perform measurements on individual single crystals. In general, single crystals are acoustically anisotropic (even those belonging to the cubic crystal system), and measurements must be made in several crystallographic directions to completely specify the elastic behavior. Hooke's law for a crystal of arbitrary symmetry is given as

$$\sigma_{ij} = c_{ijkl} \varepsilon_{kl} \quad [3]$$

where σ_{ij} is the generalized stress tensor, ε_{kl} is the strain tensor, and c_{ijkl} are the elastic stiffness constants, which we refer to here as the single-crystal elastic moduli (Nye, 1985). The Einstein summation notation is assumed, with the indices $i, j, k, l = 1 \rightarrow 3$. Alternatively, the relation between elastic strain and stress can be expressed as

$$\varepsilon_{ij} = s_{ijkl} \sigma_{kl} \quad [4]$$

where s_{ijkl} are the elastic compliances. In practice, it is the elastic stiffness, c , that is most often measured. The equations of motion for propagating elastic waves lead to the Christoffel equation:

$$\det |c_{ijkl} n_j n_l - \rho v^2 \delta_{ik}| = 0 \quad [5]$$

where n_i are components of the wave normals and δ_{ik} is the Kronecker delta (Musgrave, 1970). Equation [5] shows that the single-crystal elastic moduli can be obtained by performing measurements of sound velocities, v , with specific polarizations of particle motion and propagation directions. Depending on the specific measurement technique and quality of samples, single-crystal moduli can be determined with the highest degree of accuracy of all elastic properties. Knowledge of the c_{ij} 's also gives the elastic anisotropy of crystals and allows one to calculate the acoustic anisotropy of a polycrystal with oriented grains. However, the single-crystal moduli do not yield unique values for the aggregate elastic moduli, except for the single case of the bulk modulus of a single-phase aggregate of grains with cubic symmetry. Theoretical models of the deformation of aggregates, such as the commonly used Voigt and Reuss or Hashin and Shtrikman bounds, can only provide upper and lower bounds on the elastic moduli (e.g., Watt et al., 1976). For aggregates with grain size down to near nanometers region, the aggregate elastic properties could differ significantly from the usual averaging scheme after taking account of porosity (e.g., Chen et al., 2009; Yeheskel et al., 2005). For mantle rock aggregates with μm to mm grain size, depending on the anisotropy of a material, or the contrast in properties among the constituents of a polyphase aggregate, the uncertainties associated with calculating the properties of an aggregate can be an appreciable part of the total uncertainty in the properties of a mineral assemblage.

Of the various techniques used to measure single-crystal elastic properties, the most familiar of those used in geophysics fall into one of two categories. In an ultrasonic experiment, acoustic excitations in the sample are externally generated,

usually by means of transducers. The other type of technique is scattering experiments, where one measures the scattering of photons from acoustic phonons that are present in a sample at temperatures well above absolute zero temperature. The probe in this latter type of measurements can be a monochromatic laser beam or synchrotron x-ray beam. With the development of highly monochromatic and energetic x-ray sources at third-generation synchrotrons, along with high-energy-resolution detection, synchrotron x-rays are being more widely utilized as a means of measuring the elastic properties of Earth materials at high pressures and temperatures (e.g., Alp et al., 2001; Burkel, 2000; Fiquet et al., 2004).

2.12.2 Static Compression

The most direct and oldest method of measuring an elastic property is by static compression. If a material is compressed hydrostatically and the volume change is measured, then the isothermal bulk modulus, K_T , is determined by the definition given in the preceding text. A variety of methods have been used to generate pressure and to measure the volume, some of the more common of which are described in the succeeding text. When used with a heater of some sort, compression experiments give the P-V-T equation of state of a material.

In an isothermal static compression experiment, the P-V data are fitted with an equation of state, and the results are commonly given in terms of the bulk modulus evaluated at zero pressure, K_{0T} , and its pressure derivative (also evaluated at zero pressure) $K'_{0T} = (\partial K_{0T} / \partial P)_T$. Perhaps the most commonly used equation for fitting isothermal P-V measurements is the Birch-Murnaghan Eulerian finite-strain equation of state (Birch, 1978):

$$P = 3f(1 + 2f)^{5/2} K_{0T} (1 + x_1 f + x_2 f^2 + \dots) \quad [6]$$

where $f = 1/2((V/V_0)^{2/3} - 1)$ is the Eulerian finite strain parameter and the coefficients are $x_1 = 3/2(K'_{0T} - 4)$ and $x_2 = 3/2[K_{0T}K''_{0T} + K'_{0T}(K_{0T} - 7) + 143/9]$. In practice, K'_{0T} and higher-order derivatives typically cannot be resolved, either because the P-V data are not sufficiently precise or because they are not obtained over a large enough pressure range. This makes it reasonable to truncate the series in eqn [6] after the term $x_1 f$. In addition, it is common to assume that $K'_{0T} = 4$, further simplifying eqn [6] and data analysis. This assumption is somewhat justified by the observation that for many materials, K'_{0T} is approximately 4, but this is far from the case for many important minerals, such as garnets, rutile-structured oxides, hydrous silicates, and enstatite (see Bass, 1995). When one further considers the strong trade-off of covariance between K_{0T} and K'_{0T} (Angel, 2000; Bass et al., 1981), the approximation $K'_{0T} = 4$ can often lead to highly misleading results. Another equation of state that has become commonly used in recent years is the Vinet 'universal' equation of state (Vinet et al., 1987): $P = 3K_{0T}(V_0/V)^{2/3} [1 - (V/V_0)^{1/3} \exp\{3/2(K'_{0T} - 1)[1 - (V/V_0)^{1/3}]\}]$. Discussions of various aspects of equations of state in geophysics are given by Angel (2000), Poirier (2000), and Stacey (2005). A comprehensive review of static compression results obtained before 1995 is given by Knittle (1995). We now turn our attention to some of the methods of static compression.

2.12.2.1 Piston–Cylinder Apparatus

In its simplest form, a sample is placed in a steel or Tungsten Carbide (WC) cylinder and is compressed by pistons that advance into the two ends of the cylinder. The sample volume at high pressure is measured by the displacement of the piston, and the force applied to the piston is used to calculate the pressure. Friction between the piston and cylinder, as well as other frictional effects, needs to be accounted for in calculating an accurate pressure (Gettling, 1998). Since confined uniaxial compression of a solid (i.e., the pistons directly compressing the sample) is not hydrostatic, the sample is surrounded by a fluid pressure medium (a pentane–isopentane mixture is often used or, more recently, argon; Figure 1) for truly hydrostatic work up to ~ 3 GPa. Above this pressure, a soft solid medium is used to provide ‘quasihydrostatic’ conditions around the sample. Soft metals like Pb or, more commonly, weak minerals like talc or pyrophyllite are used as pressure media. The piston–cylinder method was used extensively in the early days of high-pressure research, and the compression of a wide variety of elements and chemically complex materials was studied with this method (most notably by P. W. Bridgman; see Bridgman, 1964). Because much higher pressures are attainable using other instruments, the piston–cylinder technique has been

used less for equation of state but more for petrology-related studies (e.g., Huang et al., 2009) in recent years.

2.12.2.2 Diamond Anvil Cell

Over the past few decades, perhaps the most commonly used instrument for measuring high-pressure equations of state has been the diamond anvil cell (DAC). This device is capable of producing the highest pressures of any static compression device, reaching the pressures found deep within the Earth’s core (e.g., Kuwayama et al., 2008; Mao et al., 1990). The DAC is also an incredibly versatile instrument. With the DAC, pressure is exerted on a sample by the small culet surfaces of two gem-quality diamonds (Figure 2). In a vast majority of equation-of-state experiments, the volume is obtained by x-ray diffraction (XRD) measurements of the distance, d , between lattice planes, using Bragg’s law: $n\lambda = 2d \sin \theta$. Both angle-dispersive XRD (using either an imaging plate or charge-coupled device (CCD) detector; Figure 2) and energy-dispersive XRD are used for volume measurements. By exerting a moderate force over the small area of the diamond tips, pressures up to several hundreds of GPa can be attained (greater than the pressure at the Earth’s center of ~ 364 GPa).

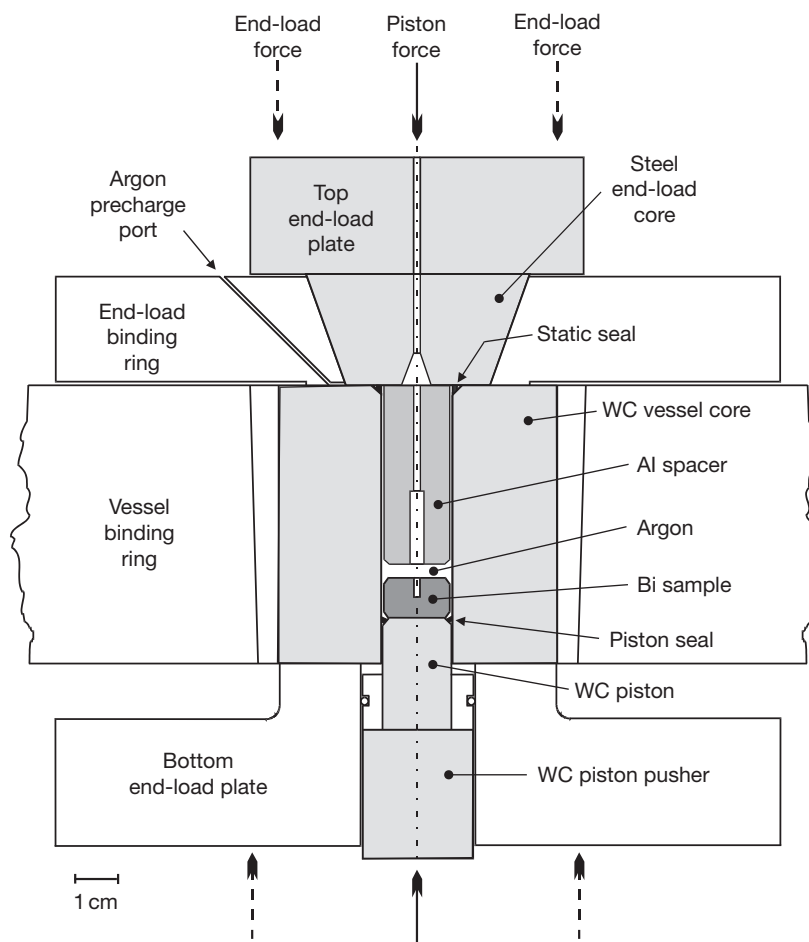


Figure 1 A modern piston–cylinder apparatus. In this particular device, hydrostatic pressure is transmitted to the sample by argon gas. Courtesy of I. Gettling.

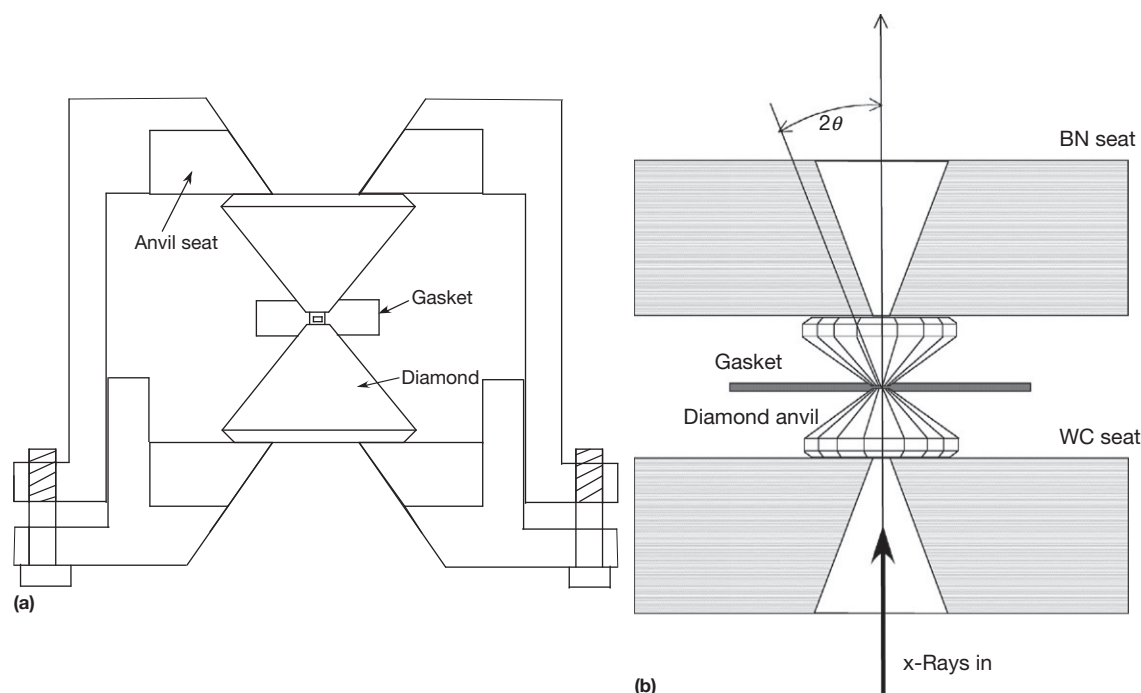


Figure 2 (a) Schematic of a piston-cylinder diamond anvil cell. The sample is between the diamonds, within a hole in the gasket (sample chamber). Screws are used to drive the diamond anvils toward each other to produce high pressure. (b) The basis for x-ray diffraction with diamond anvil cell (DAC). An x-ray beam hits the sample and diffraction is observed at various angles of 2θ . The boron nitride (BN) seat is transparent to x-rays, allowing them to be recorded on a 2D detector. These x-ray measurements yield the unit cell sample volume and density of the sample. (b) Courtesy of G. Shen.

The diameter of the culet surface is typically from 0.1 to 1 mm or more, depending on the desired pressure range. When the diamonds squeeze on the sample directly, for example, compressing a metal foil, extremely large deviatoric stresses are exerted on the sample. To help reduce this effect, the diamonds can instead compress a sample chamber consisting of a hole in a thin metal gasket, transmitting pressure to the sample via a soft pressure-transmitting medium. The best pressure-transmitting media are those with the least strength (He or Ne loaded as pressurized gasses). The choice of pressure medium is important because the presence of shear stresses and stress gradients in the sample chamber can lead to systematic errors in the measurements of pressure and volume. A detailed review of DAC technology and techniques is given by Jayaraman (1983). The newly developed radial XRD combined with DAC without any pressure medium can provide information on lattice-preferred orientation (e.g., Liermann et al., 2009; Merkel et al., 2007).

Pressure is most often measured indirectly via the fluorescence wavelengths of ruby, which are strongly pressure-dependent (Chijioke et al., 2005; Holzapfel, 2003; Mao et al., 1986). Pressure scales based on the fluorescence of other materials are also used (e.g., Datchi et al., 1997), especially at elevated temperatures. One can also use the lattice parameters or unit cell volumes of a material that is unlikely to react with a sample. The most commonly used internal standards for this purpose are MgO (e.g., Speziale et al., 2001), Au (Anderson et al., 1989; Jamieson et al., 1982), or Pt (Holmes et al., 1989) (see also Dewaele et al., 2004). At pressures above 10 or 15 GPa, uncertainties in pressure may be on the order of 10% (Fei et al., 2004; Li et al., 2005). At pressures above 30 GPa,

uncertainties in pressure are likely the largest source of error in P-V equations of state, especially using a pressure-transmitting medium with significant shear strength (or worse yet, if no pressure medium is used at all). Comparison of different pressure standards is essential for future studies (Dorfman et al., 2012).

The DAC can be used to obtain the full P-V-T equation of state when coupled with a heater. Resistance heaters (e.g., Bassett et al., 1993; Fei, 1999) provide a relatively homogenous environment in which temperature can be accurately measured with thermocouples but are usually limited in temperature to less than about 1000 °C.

Recent developments in external resistance heating have focused on new heater materials that can perform at higher temperature (e.g., graphite) and also new gasket materials that exhibit less weakening under simultaneous high-temperature and high-pressure conditions (e.g., amorphous boron) (see Liermann et al., 2009). A resistance heater inside the sample chamber of the DAC has been devised for much higher-temperature measurements to 3000 K (Zha and Bassett, 2003). The alternative method is to use laser heating, usually with a YAG (wavelength $\lambda = 1.06 \mu\text{m}$) or CO₂ ($\lambda \sim 10 \mu\text{m}$, e.g., Yagi and Susaki, 1992) laser. A YAG, YLF, or similar laser is used for heating Fe-bearing silicates or other dark, absorbing samples (e.g., metal). Transparent samples can be heated with a YAG laser by mixing them with an inert absorber, such as graphite or platinum black. An advantage of CO₂ laser heating is that the radiation from a CO₂ laser is absorbed by most transparent oxides and silicates (e.g., Fiquet et al., 1996; Yagi and Susaki, 1992). Axial temperature gradients within the sample chamber can be reduced through the use of

double-sided laser heating (Figure 3; Meng et al., 2006; Shen et al., 2001), whereas the use of a 'flat-top' or 'pi' beam shaper can reduce lateral temperature gradients (Prakapenka et al., 2008). The greatest advantage of laser heating is that it allows temperatures of several thousands of Kelvin to be obtained while at high pressure. However, the thermal pressure in the DAC is substantial but difficult to characterize (Andrault et al., 1998; Fiquet et al., 1996, 1998). Temperatures are measured using the thermal 'gray-body' radiation from the sample, from which a color temperature is obtained via Planck's radiation function (e.g., Sweeney and Heinz, 1993). Although the accurate measurement of pressure and temperature remain a significant challenge, the laser-heated DAC offers a way to maintain extreme static pressure and temperature conditions so that a variety of types of elasticity measurements can be made. Descriptions of modern beam lines developed specifically for high-pressure, high-temperature research are described by Mezouar et al. (2005) and Meng et al. (2006).

The simplicity of the diamond anvil pressure cell makes it a highly versatile device for a wide variety of spectroscopic studies and measurements of elasticity, phase relations, and a host of other properties. For example, studies of how phase transitions have shown that grain size reduction to the nanometers scale can either increase (e.g., CdSe, Chen et al., 1997) or decrease (e.g., CeO₂, Wang et al., 2001) the transition pressure of pressure-induced solid-solid phase transitions significantly (Tolbert and Alivisatos, 1995). In this section, we have described the application of the diamond anvil cell to XRD studies of the P-V-T equation of state. Other applications of the DAC for the measurement of elastic properties by spectroscopic methods (e.g., Brillouin scattering and inelastic x-ray scattering (IXS)) will be mentioned in the following sections.

2.12.2.3 Multianvil Devices

Although the DAC can attain the highest static pressures, other devices have been developed for compression studies using greater quantities of sample. One class of devices that have found widespread use for this purpose is multianvil presses. These devices can hold much larger sample volumes, approximately 1 mm³ or larger; can provide relatively uniform heating of a sample; and can accommodate a thermocouple inside the sample chamber. Figure 4 shows a diagram of a single-stage pressure device with six anvils compressing the sample assembly along the directions of the faces on a cube (a 'cube-anvil' or DIA apparatus). The sample is situated at the center of a cube-shaped pressure-transmitting assembly that may contain a heater and a soft pressure-transmitting medium immediately around the sample (Wang et al., 1996). A modified deformation-DIA apparatus (or D-DIA) was developed for high-pressure, high-temperature rheology experiments. With the D-DIA, by force exerted by the four anvils in the horizontal plane is different from the force generated by two vertical anvils, thereby producing a controlled differential stress on the sample (Wang et al., 2003). Most equation-of-state studies with single-stage devices like the DIA apparatus have been carried at pressures of about 10–15 GPa, many with simultaneous high temperatures.

Higher pressures and temperatures can be obtained with several variants of the two-stage multianvil device designed by Kawai and Endo (1970). An outer first stage of six steel anvils advances eight tungsten carbide or sintered diamond inner anvils, which in turn compress the sample assembly (see section in the preceding text on ultrasonics with this apparatus). The inner corners of the eight second-stage anvils are truncated to form an octahedral cavity in which the sample assembly is situated and compressed. As with the DIA apparatus, x-rays are

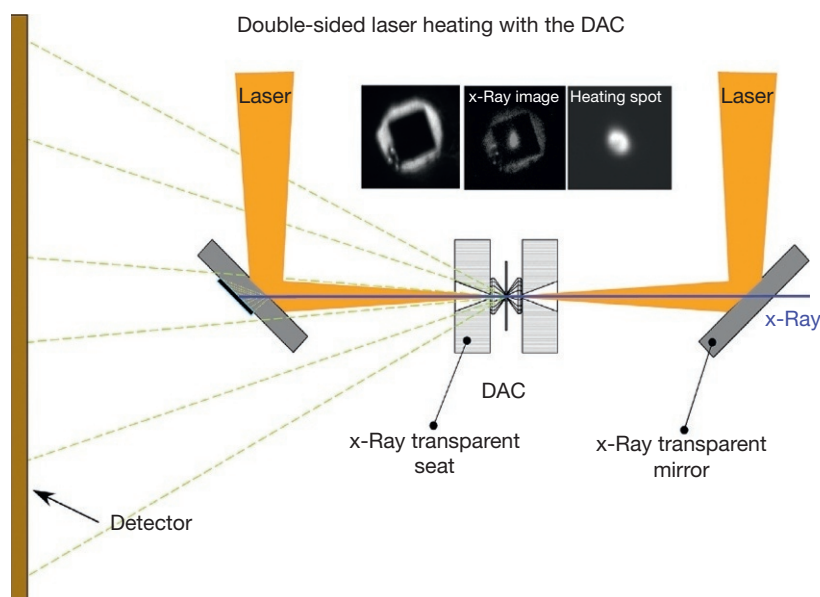


Figure 3 Laser heating with the DAC and x-ray diffraction. Lasers irradiate the sample from both sides to obtain more uniform heating of the sample and smaller thermal gradients. The photographic images show the position of the focused x-ray beam and the laser-heated spot. In this way, the P-V-T equation of state of a sample can be determined. Courtesy of G. Shen.

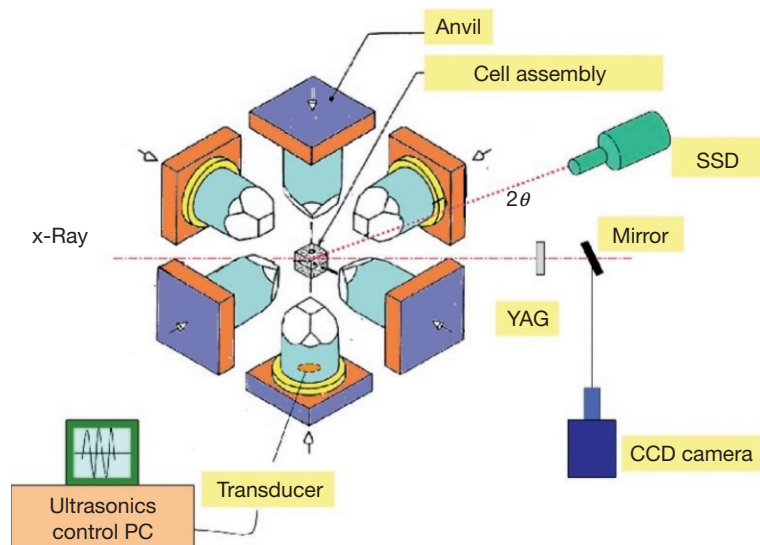


Figure 4 A single-stage six-anvil or cubic anvil apparatus used for P–V studies with synchrotron radiation and ultrasonic interferometry. x-Rays are introduced through the small spaces between the anvils, and diffracted signals can be measured through these gaps as well. The sample volume is measured by energy-dispersive x-ray diffraction recorded on a solid-state detector (SSD). A second measurement of the sample length (and hence volume) is made using x-ray radiographic images (shadowgraphs) using a fluorescent YAG crystal and CCD camera. Courtesy of B. Li.

introduced into the sample area via gaps between all the anvils. Diffracted x-rays are collected in energy-dispersive mode, giving the information needed to determine the volume of the sample at pressure via an internal calibration standard. The pressure achievable with this apparatus depends on the truncation angle of the inner stage cubes, with smaller truncations yielding greater pressures. The use of sintered diamond anvils can also extend the upper pressure limit. The achievable pressure has been increased to near 1 Mbar with larger sintered diamond anvils (Irifune, 2002; Tange et al., 2008, 2009). A recent review on the multianvil press techniques is given by Liebermann (2011).

2.12.3 Ultrasonic Methods

Ultrasonic methods are those in which a transducer is used either to produce an acoustic wave that propagates through the sample or to set the sample into vibration at its resonant frequencies. In their various forms, both methods have been used since the 1940s for the measurements of the adiabatic elastic properties of both single crystals and polycrystalline materials at elevated pressures and temperatures. These are mature experimental techniques that are in use in many laboratories around the world.

2.12.3.1 Ultrasonic Wave Transmission Techniques

Experimental methods that utilize transmitted acoustic pulses are the most precise methods available. The basis for all of the methods outlined in the succeeding text is the measurement of the travel time of an ultrasonic plane wave through a sample. Knowing the length of the sample and the travel time, the

phase velocity of the ultrasonic wave is defined. Precision on the order of several parts in 10^4 or better can be achieved in favorable cases. When applied to single crystals, ultrasonic transmission techniques are the most accurate and precise of all methods to measure elastic moduli. However, with imperfect specimens, especially polycrystalline samples or with very small samples, the accuracy of the method is not as high. The frequencies used in ultrasonic measurements typically range from hundreds of kHz to GHz. In general, the sample should be as large as possible to minimize possible systematic errors and to increase precision. Working with smaller samples, which is clearly a priority for geophysical research at high pressures, requires that the frequency of the ultrasonic probe be increased (thereby decreasing the wavelength).

Studies of single crystals by ultrasonic interferometry, as well as other acoustical techniques such as Brillouin scattering, require that sound velocities be measured in several crystallographic directions in order to determine all of the single-crystal elastic moduli. The number of velocity measurements needed depends on the symmetry of the sample, with lower symmetry materials requiring measurements in a greater number of crystallographic directions (Musgrave, 1970; Nye, 1985). For example, cubic crystals have only three independent and nonzero elastic moduli, whereas monoclinic crystals have 13. In addition, separate transducers may be required for the measurements of longitudinal and transverse waves. For each direction in which a velocity measurement is required, parallel surfaces with near perfect flatness must be prepared. Measurements on isotropic aggregates of randomly oriented crystallites require only one measurement, each of longitudinal and transverse wave velocities, and yield the aggregate elastic properties directly. However, these advantages are offset by decreased accuracy due to the imperfections often present in polycrystalline materials (e.g., cracks, pores, and preferred orientations of grains). Hot pressing and sintering of polycrystalline materials under elevated

pressure and temperatures can greatly minimize these effects by producing polycrystalline materials with few imperfections and of near theoretical density (Gwanmesia et al., 1993). One of the powerful advantages of ultrasonic methods is that they can be used with almost any type of sample.

2.12.3.1.1 Pulse transmission

The pulse transmission technique is the simplest for measuring elastic properties by ultrasonics. A transducer at one end of a sample converts an electrical impulse from a pulse generator into a mechanical or acoustic pulse in the sample. The essential elements of the experimental setup are shown in Figure 5. A transducer at the opposite end of the sample senses the transmitted acoustic wave and converts it into an electrical signal that can be recorded and timed. The travel time through the specimen is thus determined, and, with the known length of the sample, a velocity can be calculated.

Although of lower precision than some other ultrasonic methods, the pulse transmission technique is highly versatile, simple, and especially useful for characterizing the properties of rocks and highly attenuating samples. Low frequencies in the range a few kHz to MHz allow one to perform measurements on coarse-grained rocks and other types of samples for which scattering of high-frequency waves would be problematic. This technique was used by Birch (1960) and Simmons (1964) in their classic studies of the P and S velocities in a variety of rocks to 10 kilobars. A comprehensive summary of measurements performed on a variety of geologic materials, including sediments, dry and fluid-bearing rocks, and other aggregates, is given by Christensen (1982). This method has continued to find use in characterizing the velocities, elastic moduli, and attenuation in a wide range of geologic materials (e.g., Prasad and Manghnani, 1997; Vanorio et al., 2003; Vialle and Vanorio, 2011).

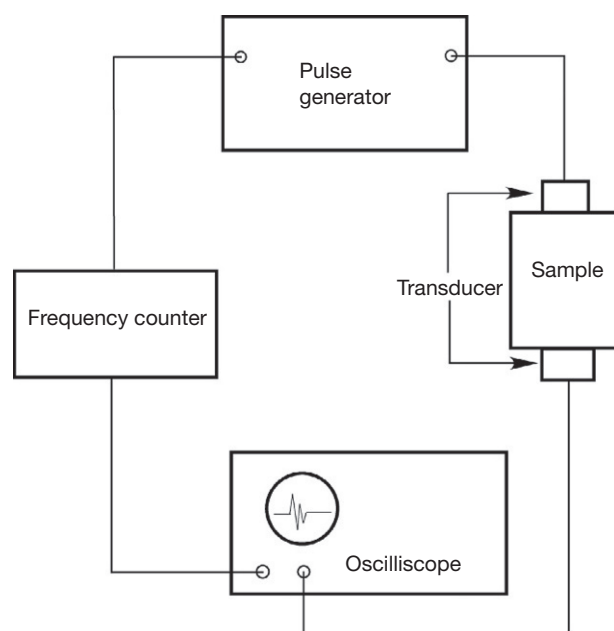


Figure 5 Schematic of a pulse transmission experiments. The transducer attached to the top of the sample produces an ultrasonic pulse, and the bottom transducer receives the transmitted signal.

2.12.3.1.2 Ultrasonic echo methods

In cases where high-quality single crystals or fine-grained polycrystalline samples are available, highly precise measurements of elastic properties can be made by using multiple reflections of acoustic waves, or echoes, within a sample. The various methods developed around this concept involve measuring the time interval between successive echoes or the phase delay between two echoes of a monochromatic acoustic wave train. Three methods commonly used are the pulse-echo overlap, pulse superposition, and phase comparison methods. These methods are more accurate and precise than the pulse transmission method, and, in cases where high-quality samples are available, pulse-echo methods are often viewed as the gold standard for elastic wave velocity and elastic modulus measurements. Very often, 'buffer rods' are placed on either end of the sample, separating the sample and transducer. This can serve to simply place the transducer away from the sample environment, which is necessary in most high-pressure or high-temperature experiments. In addition, the use of buffer rods can minimize errors introduced by changes in phase of the ultrasonic waves as they reflect from the ends of the sample (Davies and O'Connell, 1977; Jackson et al., 1981; McSkimin, 1950). A WC buffer rod, arranged as it is used in a modern high-pressure experiment, is shown in Figure 6.

In the pulse-echo overlap technique (Papadakis, 1967, 1990), individual pulses are excited in a sample and the same transducer is used to detect reflections. The timing of the pulses is long enough that each pulse undergoes multiple reflections and attenuates before a new pulse is introduced. The relative phases of two successive echoes are adjusted so that they align, or overlap, via the triggering rate of an oscilloscope. The triggering frequency needed to overlap echoes is equal to the reciprocal of the travel time in the sample. The measured travel time, T , is then equal to

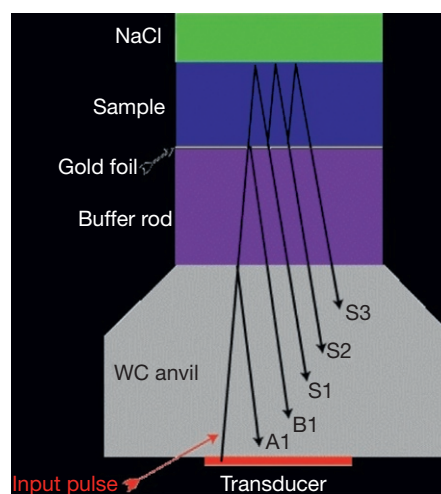


Figure 6 Ultrasonic pulses and echoes in a modern high-pressure experiment. The transducer is mounted on a pressure-generating anvil. A buffer rod separates the transducer from the sample embedded in a pressurized medium. Reflections or echoes from ends of the sample are indicated. Courtesy of W. Liu and R. C. Liebermann.

$$T = pT_0 - \frac{p\gamma}{2\pi f} + \frac{n}{f} \quad [7]$$

where T_0 is the intrinsic round-trip travel time in the sample, p is the number of round trips between reflections, γ is the transducer bond phase shift, f is the frequency of the ultrasonic wave, and n is an integer related to the number of cycles of mismatch in the overlap of a wave train (Papadakis, 1967). Assuming that the phase shift γ is independent of frequency, it can be determined through measurements at slightly different frequencies (McSkimin, 1961; Papadakis, 1967).

With the pulse superposition technique (McSkimin, 1961), the repetition rate of the radio frequency pulse generator is varied such that it coincides with the arrival of an echo or some integral number (p) of echo intervals (i.e., every second echo or every third echo). When the timing of the pulses is precisely equal to the time between echoes (i.e., the round-trip travel time through the specimen), then the amplitude of echoes viewed on an oscilloscope will be at a maximum. Equation [7] can then be used to determine the true travel time in the specimen. Clearly, it is advantageous to use large samples because this makes T_0 larger relative to the other terms in eqn [7], minimizing errors due to the uncertainties in the measurements of γ , T , and the length of the sample.

With the phase comparison method (Jackson and Niesler, 1982; McSkimin, 1950; Niesler and Jackson, 1989), the main experimental variable is the frequency of the ultrasonic wave in the sample. Coherent sinusoidal pulses of frequency f are excited in the sample. The frequency of the ultrasonic waves is varied so that successive echoes are in phase and display a constructive interference maximum or, alternately, destructively interfere to yield a minimum in amplitude. The velocity of the propagating ultrasonic wave is then

$$V_0 = \frac{2lf_0}{n + (\gamma/2\pi)} \quad [8]$$

where l is the sample thickness, f_0 is the frequency for maximum constructive interference, n is an integer equal to the number of cycles in the sample at f_0 , and γ is the phase angle defined previously. The integer n can be determined by sweeping the frequency through consecutive maxima (or minima, which may be detected with more certainty). The phase comparison method has been used extensively in high-pressure studies of minerals (e.g., Jackson and Niesler, 1982; Niesler and Jackson, 1989), making it a valuable tool in geophysical research. When used with single crystals, it is considered to be one of, if not the most accurate technique for obtaining elastic properties at high pressure.

The time required to perform a pulse-echo ultrasonic experiment has been greatly reduced through the development of the 'transfer function' method (Li et al., 2002, 2004). Instead of sweeping through a range of frequencies, as in the pulse-echo overlap or phase comparison methods, a broadband pulse is introduced to the buffer rod and sample, and the received signal $y(t)$ is recorded digitally. Knowing the input pulse, $x(t)$, and the received signal, the system response, $h(t)$, of the transducer-buffer rod-sample assembly is therefore defined at all frequencies simultaneously from the relation $y(t) = x(t) \times h(t)$. The Fourier transform of the input and output signals can be expressed as $Y(f) = X(f) \times H(f)$, where

$H(f) = Y(f)/X(f)$ is the transfer function. In essence, the transfer function contains information on the response of the system over a broad range of frequencies (typically several 10s of MHz), and it is acquired in a single, fast recording. From the transfer function, one can reproduce the received signal of a monochromatic pulse of any given frequency within the frequency band of the source. Thus, one can reproduce the monochromatic pulse-echo overlap or phase comparison experiments and calculate travel times accordingly. With this technique, the frequency response of the system can be obtained in seconds, as opposed to the several minutes typically required to scan in frequency using, for example, the conventional phase comparison method. The speed of the transfer method makes it possible to study kinetics and other time-dependent phenomena.

2.12.3.2 High-Pressure Ultrasonics

Ultrasonic echo methods have been used extensively for measuring elastic moduli at high pressures and temperatures, employing a variety of high-pressure devices. As noted in the preceding text, phase comparison has been one of the more commonly used methods for determinations of elastic properties at high pressure. Jackson and Niesler (1982) developed a method whereby a transducer is bonded directly to a sample, and the entire assembly is compressed in a piston-cylinder apparatus. Hydrostatic pressure is transmitted to the sample via a liquid (a pentane-isopentane mixture is commonly used), thus eliminating errors due to deviatoric stresses on the sample. Pressure is measured via the electrical resistance of a manganin wire. While this is a relatively accurate method for high-pressure elastic modulus measurements, it is limited to pressures of about 3 GPa.

The pressure limitations of the piston-cylinder apparatus and fluid pressure media are overcome by using a solid pressure medium and a multianvil apparatus. By using a soft material such as NaCl for transmitting pressure to the sample and annealing the sample and pressure medium assembly to relax deviatoric stresses, quasihydrostatic conditions can be attained on samples at high pressure (Weidner et al., 1992). The two types of multianvil apparatuses being used for high-pressure ultrasonics are a single-stage cubic anvil (DIA) system (Figure 4; Li et al., 2004; Weidner et al., 1992) and the two-stage Kawai-type multianvil apparatus (Figure 7; Kawai and Endo, 1970; Uchida et al., 2002). In the case of the two-stage apparatus, which can reach higher pressures, eight WC anvils with truncated corners surround an octahedral sample chamber containing the sample assembly (Figure 8). The transducer is attached to the outer truncated corner of an anvil, which thus serves as a buffer rod. Ultrasonic pulses are then transmitted to the sample by another buffer rod between the WC anvil and the sample (Figure 8). When the WC cubes are driven together by six outer or 'first-stage' anvils (not shown in Figure 7; see Kawai and Endo, 1970; Uchida et al., 2002), pressures of >20 GPa can be attained. A heater in the sample assembly allows simultaneous temperatures of >1200 °C (Higo et al., 2006). Changes in the sample length, required for accurate velocity determinations, are measured directly using synchrotron x-ray radiography. A synchrotron x-ray beam is directed through the space between the WC anvils, and the transmitted

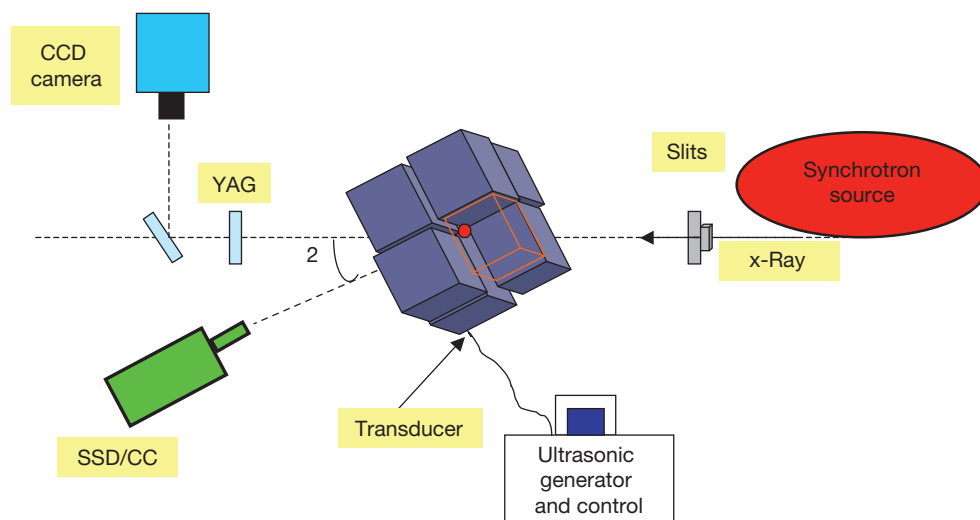


Figure 7 Schematic diagram of the setup for ultrasonics in a Kawai-type multianvil apparatus. The YAG crystal and CCD camera are for x-ray radiography of the sample to determine its length in situ. The solid-state detector is used for energy-dispersive x-ray diffraction. The transducer that produces an ultrasonic signal is attached to one of the WC cubes that acts as a primary buffer rod. Adapted from Vaughan MT, Weidner DJ, Wang Y, Chen J, Koleda CC, and Getting IC (1998) T-CUP: A new high-pressure apparatus for X-ray studies. *Review of High Pressure Science and Technology* 7: 1520–1522; Li B, Kung J, Uchida T, and Wang Y (2005) Pressure calibration to 20 GPa by simultaneous use of ultrasonic and X-ray techniques. *Journal of Applied Physics* 98. <http://dx.doi.org/013521-1-013521-5>.

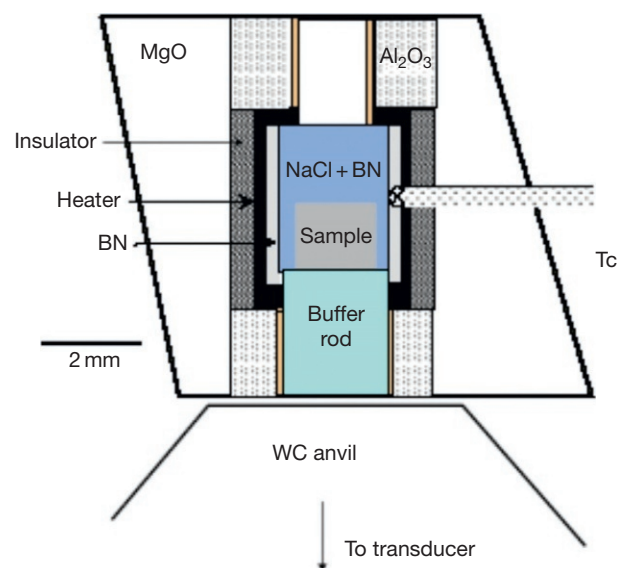


Figure 8 Sample assembly used for ultrasonic velocity measurement experiments at high pressure in a Kawai-type multianvil apparatus. Adapted from Kung J, Li B, Uchida T, Wang Y, Neuville D, and Liebermann RC (2004) In situ measurements of sound velocities and densities across the orthopyroxene-high-pressure clinopyroxene transition in MgSiO_3 at high pressure. *Physics of the Earth and Planetary Interiors* 147: 27–44; Li B, Kung J, Uchida T, and Wang Y (2005) Pressure calibration to 20 GPa by simultaneous use of ultrasonic and X-ray techniques. *Journal of Applied Physics* 98. <http://dx.doi.org/013521-1-013521-5>.

beam is recorded via a YAG crystal (serving as a fluorescent screen) and detector. Due to their high absorption, the images of metal markers (typically Au foil) on either side of the sample are apparent in this x-ray radiograph and give the sample

length directly. Because this device allows velocity, sample length, and, hence, volume to be measured in a single experiment, it is possible to obtain the pressure on the sample directly (Ruoff et al., 1973). This remarkable apparatus illustrates the flexibility in adapting ultrasonic methods to a variety of high-pressure devices, due in part to the ability to introduce the signal to the sample via buffer rods.

Ultrasonic measurements of velocities have also been carried out in a toroidal anvil apparatus (Khvostantsev et al., 2004), a device in which pressure is generated by two opposed curved anvils. This device can generate pressures to ~ 15 GPa on relatively large sample volumes, with high temperatures. Ultrasonic measurements with the toroidal cell date back to the work of F. F. Voronov in the mid-1970s (see the review by Khvostantsev et al., 2004). This technology continues to be developed and has more recently combined synchrotron XRD with ultrasonic capabilities (Lheureux et al., 2000).

In an attempt to perform ultrasonic velocity measurements to even higher pressures, an ultrasonic interferometer has been devised for use with the DAC. The challenge in this experiment is the small sample thickness in a DAC (typically less than $50 \mu\text{m}$, in comparison with ~ 1 mm in a multianvil device). Such thin samples require higher-frequency ultrasound waves. This emerging technique has proven successful in measuring both longitudinal and shear elastic wave propagation times in samples compressed in a DAC. Producing shear waves at the requisite GHz frequencies appropriate for samples in a DAC is problematic. An ingenious method of converting longitudinal GHz acoustic waves to transverse waves (P-to-S conversion) is achieved via reflection at a critical angle on the buffer rod (see Figure 9; Jacobsen et al., 2002). Some of the recent technical advances and results obtained with this promising new method are given by Jacobsen et al. (2004), Kantor et al. (2004), and Reichmann and Jacobsen (2006).

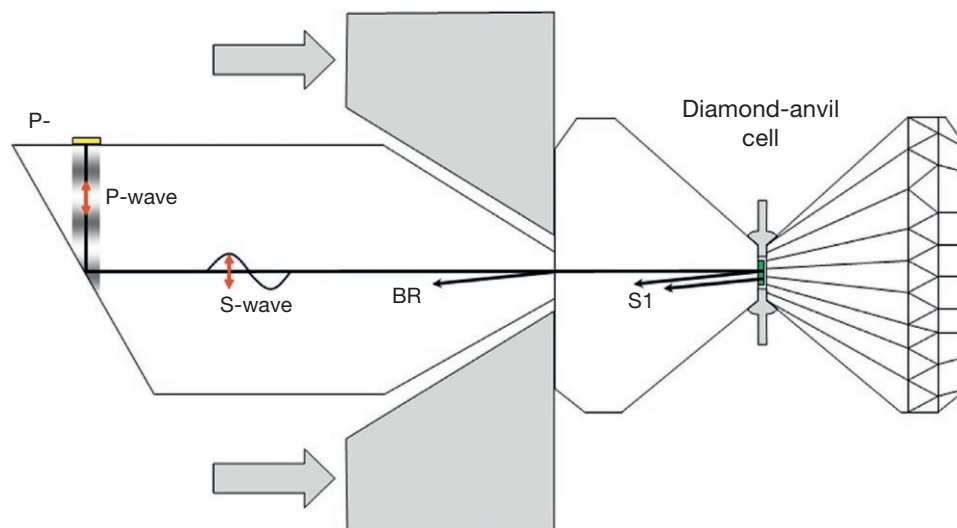


Figure 9 GHz ultrasonics with the DAC. Ultrasonic pulses are transmitted to the sample via a buffer rod and the diamond anvil on the left. The production of a shear wave is illustrated via a longitudinal-shear (P-to-S) conversion upon reflection from a polished surface on the buffer rod (Jacobsen et al., 2002a). Courtesy of S. Jacobsen.

An important application of high-temperature ultrasonics has been the measurements of the properties of silicate melts. Measurements on silicate melts are challenging because of the rather high temperatures involved (typically $>1000^\circ\text{C}$ for dry melts) and their high viscosity. The elastic properties of numerous silicate melts, spanning a broad range of compositions, were measured by Rivers and Carmichael (1987). These authors successfully employed both the pulse-echo overlap technique and an interferometric technique in their experiments. With either method, the ultrasonic waves are introduced into the high-temperature melt via a refractory buffer rod (molybdenum in this case). The sample is contained in a crucible with a flat bottom to reflect ultrasonic waves propagating through the sample. Maxima and minima in the amplitude of the ultrasonic echoes are obtained by moving the buffer rod to vary the path length in the molten sample. The distance between successive amplitude maxima or minima yields the wavelength and the velocity of sound in the liquid. The reader is referred to the works of Baidov and Kunin (1968), Murase et al. (1977), and Katahara et al. (1981), which document primary developments in this important area of research.

2.12.3.3 Vibrational Resonance

The resonant vibrational modes of a body are a function of its elastic moduli and external dimensions. The measurements of the vibrational resonance frequencies can therefore be used to obtain all of the elastic properties of a sample in a single experiment. In contrast to the ultrasonic wave transmission methods, where individual velocities are usually measured on different single-crystal samples with specific crystallographic orientations, the vibrational resonance spectrum (amplitude vs. frequency of excitation) yields all of the single-crystal elastic moduli from one experiment. An additional advantage of this technique is that it allows the use of smaller samples for a given ultrasonic frequency range or, alternatively, the use of lower

frequencies for a given size of sample (Ohno, 1976). Internal friction or attenuation (Q^{-1}) can also be measured. The technique was applied to the measurement of the bulk and shear moduli of elastically isotropic spheres by Fraser and LeCraw (1964) and Soga and Anderson (1967). Interpreting the results for anisotropic crystals, even those of cubic symmetry, is not straightforward. Since the early measurements on elastically isotropic materials, both the experimental and theoretical aspects of resonant ultrasound spectroscopy (RUS) measurements have been refined and applied primarily to high-temperature elasticity studies, including the properties of high-pressure phases at elevated temperatures.

Using RUS methods to determine the single-crystal elastic moduli of anisotropic materials is far more complex than for isotropic substances. The difficulty is mainly in the forward problem of calculating the RUS spectrum expected for an anisotropic crystal of a given shape. This difficulty exists even for crystals of the cubic crystal system, which can display a high degree of elastic anisotropy. The complexity (number of peaks) of an RUS spectrum increases as the symmetry of a material decreases and also depends on the detailed shape of a crystal. A major advance in this field was made by Demarest (1971), who solved the problem of calculating the resonant spectrum for crystals with cubic crystallographic symmetry, in the shape of a cube. Demarest's work was extended to the case of orthorhombic crystals by Ohno (1976) and more recently to monoclinic crystals (Isaak et al., 2006). The RUS spectral data are sufficiently complex that assignment of peaks to specific vibrational modes can be difficult and any misidentification of the peaks will result in erroneous elastic moduli. Having a good starting model for the elastic moduli greatly assists in the evaluation of the data.

In most recent versions of the RUS method, two transducers are attached to opposite corners of a cube or rectangular parallelepiped (Figure 10). One of the transducers is used to vibrate the sample and the other acts as a receiver. An experimental concern is the effect that the transducers have on the

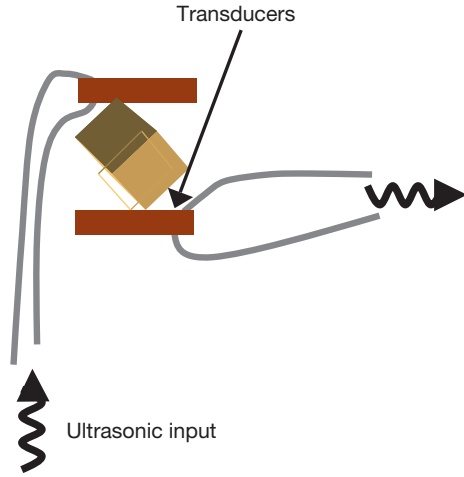


Figure 10 Schematic of a resonant ultrasound experiment. The transducers excite different resonant vibrations as the ultrasonic input is scanned in frequency. Courtesy of D. Isaak.

observed resonant frequencies. The theory for analyzing RUS spectra assumes stress-free boundaries on the sample, and the effect of the force exerted by contact with the samples cannot be accounted for theoretically. In practice, the experiment can now be done with sufficiently low stresses exerted on the sample that the effects are thought to be small relative to other sources of error. The high-temperature elastic properties of numerous materials have been measured by RUS, at temperatures as high as 1800 K (e.g., Isaak et al., 1989), and a review of much of those results has been presented by Anderson and Isaak (1995). The technique has recently been applied to the measurement of the properties of high-pressure mantle phases at high temperatures (Mayama et al., 2005).

2.12.4 Light Scattering Techniques

2.12.4.1 Brillouin Scattering

Over the past few decades, Brillouin scattering has been perhaps the most frequently used technique for the measurements of the single-crystal elastic properties of materials of geophysical interest, especially for phases that are stable only at high pressures. This is largely due to the fact that it is an optical, noncontact technique in which no coupling of transducers or other devices to the sample is needed to produce an acoustic excitation. As a result, Brillouin scattering is intrinsically suitable for measurements on small transparent or translucent samples of less than 100 μm in lateral dimensions. The ability to accurately measure the elastic properties of very small samples, either single crystals or well-sintered polycrystalline samples, without physical contact, is a strength of the Brillouin scattering technique. Brillouin scattering can be performed on samples at high pressure in a DAC and/or at high temperature. Weidner et al. (1975) first applied the Brillouin scattering technique to measurements on a small single-crystal sample of geologic importance. Since these first experiments, the technique has continued to be developed and refined for geoscience research.

Brillouin scattering is the inelastic scattering of light (photons) by thermally generated acoustic lattice vibrations (phonons). That is, incident light is scattered from acoustic lattice vibrations that result from thermal motion of atoms in a sample. This scattering changes the frequency of the scattered light by an amount that depends on the phase velocity of the acoustic wave. One way to view the process is to consider a sound wave in a material as producing a periodic modulation of the refractive index, which can scatter light. Because the modulation is propagating with the speed of sound, the scattered light is Doppler-shifted in frequency. Alternatively, the inelastic scattering process may be viewed as the creation or annihilation of a phonon by a photon.

With either model of the process, a small portion of the light scattered is shifted in frequency due to the photon-phonon interaction. If we consider incident light of wave vector k_i being scattered into a photon of wave vector k_s through interaction with a phonon of wave vector q , these wave vectors are related through conservation of momentum for the scattering process:

$$k_s - k_i = \pm q \quad [9]$$

where the + sign indicates phonon annihilation (anti-Stokes scattering) and the - sign indicates phonon creation (Stokes scattering). From conservation of energy, the frequencies in the scattering process are related by

$$\omega_s - \omega_i = \pm \Omega \quad [10]$$

where Ω is the frequency of the phonon. Because $|k_s| \cong |k_i|$, then for an optically isotropic sample and a scattering angle θ between the incident and scattered wave vectors,

$$2|k_s| \sin(\theta/2) = q \quad [11]$$

Note that the scattering angle θ refers to the angle between the incident and scattered light inside the sample, after any refraction at the sample boundaries. Because many minerals are of low symmetry and optically anisotropic, it is useful to consider the more general relation for the velocity (v) of the acoustic wave that follows from eqns [9] and [10]:

$$v = \frac{c(\omega_i - \omega_s)}{\omega_i(n_i^2 + n_s^2 - 2n_i n_s \cos \theta)^{1/2}} \quad [12]$$

where n_i and n_s are the refractive indices for the incident and scattered light, respectively, and c is the speed of light. A special case of particular interest for high-pressure measurements using the DAC is one where light enters and exits the sample at the same angle or, symmetrically, through parallel faces of a plate-shaped sample (Figure 11). In this case, if the sample is optically isotropic, the expression for the sound velocity is

$$v = \frac{4\omega \cdot \lambda}{2 \sin(\theta^*/2)} \quad [13]$$

(Whitfield et al., 1976), where θ^* is the external angle between the incoming and the scattered light directions outside of the sample (Figure 11). This scattering geometry is very convenient and commonly used because the velocities are determined independent of the refractive index of the sample and because it is compatible with DAC measurements (Figure 11). Note that eqn [13] strictly holds only for isotropic materials or when

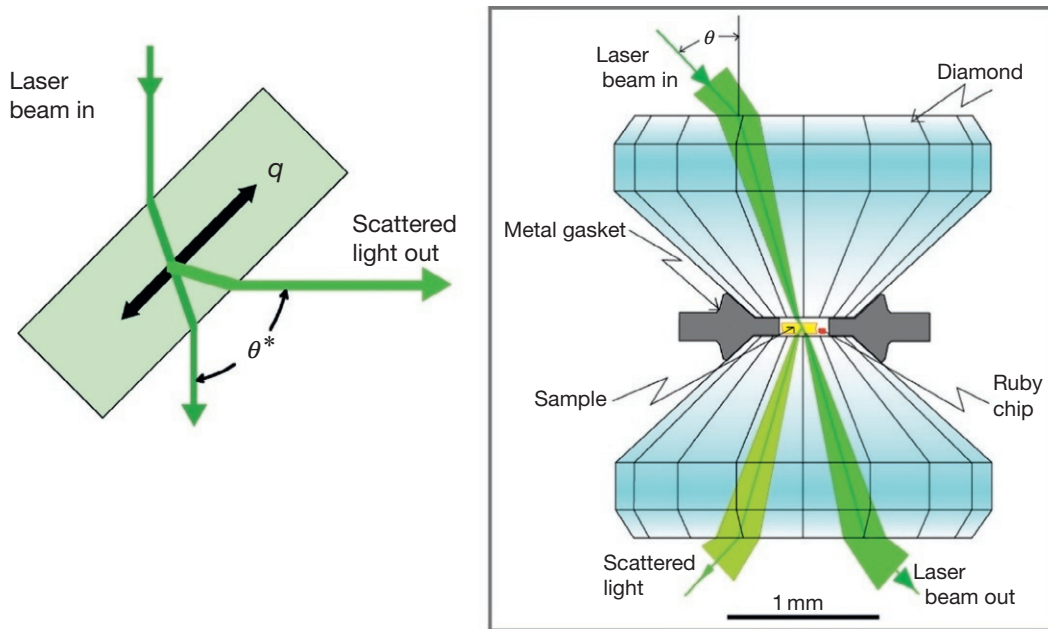


Figure 11 The left-hand panel shows the geometry of a Brillouin scattering experiment with a platelet sample in a symmetric geometry. The external scattering angle in eqn [13] is shown. The geometry is used in high-pressure Brillouin experiments with the DAC (right panel). Courtesy of S. V. Sinogeikin.

$n_i = n_s$. A backscattering geometry ($\theta = 180^\circ$) is also commonly used, and in this geometry, the observed Brillouin shift $\Delta\omega \propto nv$, thus requiring knowledge of the refractive index to obtain velocities and elastic moduli. In addition, the amplitude of the shear modes goes to zero in a backscattering geometry. An extensive review of Brillouin scattering is given by Sandercock (1982) and references therein.

A schematic of a Brillouin spectrometer is shown in Figure 12. The main component is a 6-pass Fabry-Pérot interferometer that is capable of resolving the very small frequency shift, $\Delta\omega$, of the Brillouin scattered light and the elastically scattered Raleigh light (Bass, 1989; Sandercock, 1982). This requires an instrument with very high finesse. In addition, the Fabry-Pérot must have a very high contrast (signal-to-noise ratio) for low-intensity Brillouin peaks to be above any background. Both longitudinal and shear waves are obtained using the 50° or 90° scattering geometries typically used (Figure 13). The frequencies of the acoustic waves probed by Brillouin scattering are typically in the range of tens of GHz. In a single-crystal Brillouin experiment, the orientation of the sample is changed so that velocities with many values of q are probed. In this way, sufficient data may be obtained to constrain all of the single-crystal elastic moduli. The intrinsic precision of Brillouin measurements is on the order of 0.1–0.5%, depending upon the sample. By collecting large amounts of data (velocity vs. orientation), the uncertainties in the experimental results can be reduced considerably. A generalized inversion technique can be used to obtain the single-crystal elastic modulus tensor, c_{ij} , from the velocities and phonon directions (Weidner and Carleton, 1977).

The basic strategy for carrying out a high-pressure Brillouin experiment using the DAC is described by Whitfield et al. (1976) (Figure 11). This work has been followed up by high-

pressure Brillouin studies on a variety of materials (Brody et al., 1981; Duffy et al., 1995; Polian and Grimsditch, 1984; Sinogeikin and Bass, 1999), and high-pressure Brillouin studies are now performed in a number of laboratories around the world. It is now possible to measure sound velocities to pressures of 100 GPa and above (e.g., Murakami et al., 2007). High-temperature measurements can be performed using resistance heaters to ~ 1700 K (Jackson et al., 2004; Sinogeikin et al., 2000) or with CO_2 laser heating to temperatures approaching 3000 K (Sinogeikin et al., 2004a,b). Brillouin scattering can be used to measure the surface wave velocities of metal samples (Crowhurst et al., 1999; Sandercock, 1982) and examine the elastic properties of nanocrystalline materials (e.g., MgO, Marquardt et al., 2011). Measurements at simultaneous high pressures and high temperatures are now possible using resistance heaters (Lu et al., 2013) and laser heating (Murakami et al., 2012).

A recent application of Brillouin scattering is related to the measurement of hypersonic phonon band gaps in phononic materials. Some phonons do not propagate in phononic materials, thereby offering the possibility of manipulating sound waves (Gomopoulos et al., 2010; Schneider et al., 2012) and processes that depend on high-frequency phonon propagation. The measurement of hypersonic phononic band gaps requires the measurement of phonon dispersion; this is achieved by continuously changing the scattering angle over a wide range in a Brillouin scattering experiment, from near-forward to near-backscattering geometry. Thus, the experimental setup for the measurements of phonon dispersion differs greatly from the traditional fixed scattering angle experiments.

Another new application of Brillouin scattering is its interfacing with synchrotron radiation for the simultaneous

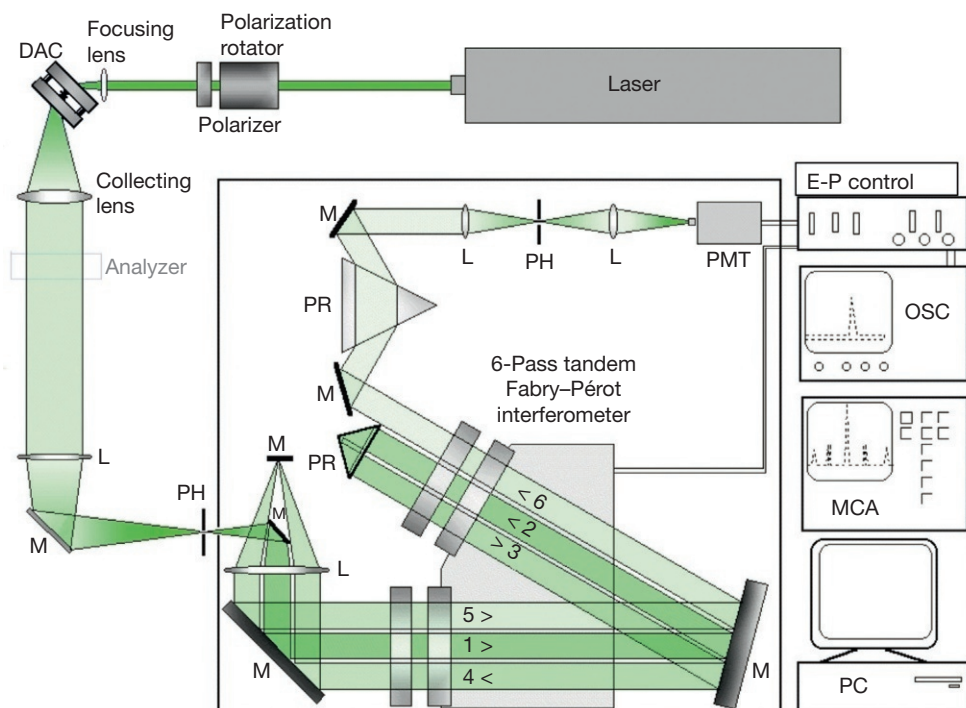


Figure 12 Schematic diagram of a Brillouin spectrometer. An orientation device such as a three-circle Eulerian cradle can be at the sample position (where a DAC is shown here), so that the sample orientation can be changed to access different phonon directions. Light scattered by the sample is analyzed by an electrically scanning Fabry-Pérot interferometer. M, mirror; L, lens; PR, prism; PH, pinhole. Courtesy of S. V. Sinogeikin.

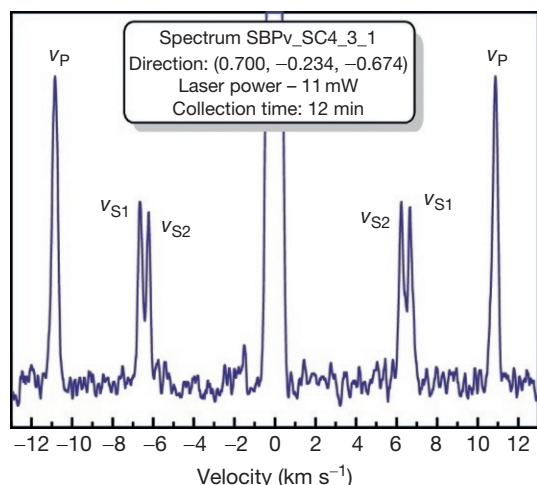


Figure 13 Brillouin scattering spectrum for the high-pressure phase MgSiO_3 perovskite. A longitudinal (v_P) and two polarizations of transverse waves (v_{S1} and v_{S2}) are shown symmetrically on either side of the strong elastic peak at zero velocity in the center of the spectrum. Courtesy of S. V. Sinogeikin. The distance of the sharp Brillouin peaks from elastic peak is proportional to the velocity. Reproduced from Sinogeikin SV, Zhang J, and Bass JD (2004) Elasticity of single crystal and polycrystalline MgSiO_3 perovskite by Brillouin spectroscopy. *Geophysical Research Letters* 31: L06620. <http://dx.doi.org/10.1029/2004GL019559>.

measurements of sound velocities and volume (density). This capability has recently been developed at the GSECARS (Sector 13) beam line of the Advanced Photon Source (Sinogeikin et al., 2006) and should allow the development of improved pressure scales for high-pressure research (Ruoff et al., 1973).

2.12.4.2 Impulsive Stimulated Scattering

Impulsive stimulated scattering (ISS) is another laser-based technique for measuring the single-crystal elastic moduli or the bulk elastic properties from polycrystalline samples. Unlike Brillouin scattering, where the scattering is from intrinsic thermal motion of the atoms, the ISS acoustic signal is produced via the interaction of interfering lasers in the sample. Thus, this method is sometimes referred to as stimulated Brillouin scattering, or laser-induced phonon spectroscopy. An advantage of the techniques is that the scattered signal is much stronger than with Brillouin scattering, but the nature of the experiment data (acoustic velocities as a function of crystallographic direction) is essentially the same as with Brillouin or ultrasonic interferometry. The ISS technique has additionally been used to measure thermal diffusivity and acoustic attenuation. The theory and applications of the ISS technique have been discussed in review papers by Abramson et al. (1999) and Fayer (1982).

The basis for the ISS technique as applied to materials of geophysical and geochemical interest has been reviewed by Brown et al. (1988), Abramson et al. (1999), and Zaug et al. (1992). With ISS, acoustic excitations are produced in a sample

by the interference of two pulses from the output of a Q-switched, mode-locked laser that are combined in a sample at an angle 2θ (Figure 14). The interference of these laser beams produces a periodic variation of intensity, which, for absorbing samples, produces a concomitant variation in temperature of the sample. The rapid appearance of this thermal grating and the associated thermal pressure excite a quasi-longitudinal and two quasitransverse acoustic waves. The wavelengths, λ_{Av} , of the thermal fluctuations and acoustic waves are equal and given by

$$d = \lambda_A = \frac{\lambda}{2 \sin(\theta)} \quad [14]$$

where λ is the wavelength of the laser light (1064 nm in this case). A third beam from the Q-switched laser is frequency-doubled, time-delayed, and scattered from the thermal grating at the Bragg angle to serve as a probe of the acoustic waves. The intensity of the probe as a function of delay time yields the frequency of the acoustic wave, ν_A , and hence its velocity. The raw data are in the time domain and Fourier-transformed to obtain the acoustic frequencies. Note that where a sample is elastically isotropic, only a longitudinal wave is excited. In cases where the sample does not absorb at the 1064 nm frequency of the interfering lasers, electrostriction may be sufficient for the excitation of acoustic phonons.

Like Brillouin scattering, ISS may be used to investigate the properties of surface waves on metals, including at high pressure (Crowhurst et al., 2003), and the elastic moduli of minerals with low symmetry (e.g., Brown et al., 2006).

2.12.5 Inelastic x-Ray Scattering

The development of intense third-generation synchrotron x-ray sources and the ability to achieve extremely high energy resolution, on the order of 1 meV, have opened the opportunity to determine sound velocities through IXS (Burkel, 2000). Here, we mention two types of IXS techniques that have recently been applied to the measurement of velocities and elastic moduli for materials of relevance to geophysics and that have been developed for high-pressure experiments with the DAC.

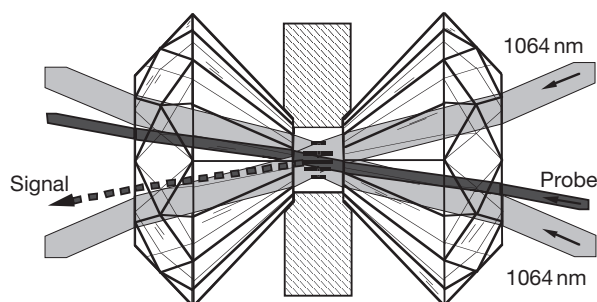


Figure 14 The impulsively stimulated scattering technique. Two laser beams enter (from the right) through the back of a diamond and cross in the sample. The transient grating produced in the sample will diffract a probe beam brought in at the Bragg angle. Courtesy of J. M. Brown.

2.12.5.1 Nuclear-Resonant Inelastic x-Ray Scattering

This technique provides a way of probing the phonon density of states (PDOS) by excitation of nuclear resonances for specific isotopes. From the density of states, sound velocities and thermodynamic properties can then be calculated. Intense synchrotron x-rays with a tightly defined energy bandwidth are used to excite the nuclear resonances. One of the optimal isotopes for nuclear-resonant inelastic x-ray scattering (NRIXS) studies is ^{57}Fe , which is fortuitous given the abundance of Fe and Fe-bearing compounds in the Earth.

The configuration of a sample for a high-pressure NRIXS experiment in a DAC is shown in [Figure 15](#). In an NRIXS experiment, short pulses of synchrotron x-rays excite fluorescent radiation from the Fe sublattice, and this fluorescence is recorded in a short time window between pulses. It is important to note that the experiment selectively probes the Fe atoms, and other elements in the sample do not contribute to the recorded signal. The energy of the impinging x-rays is scanned, typically by less than ± 100 meV in steps of ~ 0.25 meV about the nuclear transition energy of 14.4125 keV for ^{57}Fe .

Three avalanche photodiodes around the sample record a spectrum of intensity versus energy of the incident radiation,

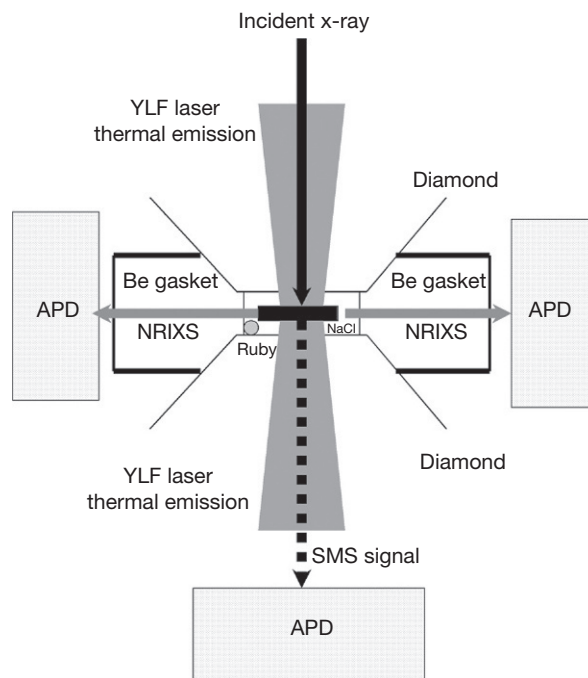


Figure 15 Experimental configuration for a nuclear-resonant inelastic x-ray scattering experiment at high pressure in the DAC. The ^{57}Fe -enriched sample is surrounded by a NaCl pressure medium within the sample chamber of an x-ray transparent Be gasket. Avalanche photodiodes (APDs) surrounding the sample to detect the nuclear-resonant signal. Reproduced from Lin JF, Sturhahn W, Zhao J, Shen G, Mao HK, and Hemley RJ (2005) Nuclear resonant inelastic X-ray scattering and synchrotron Mössbauer spectroscopy with laser-heated diamond anvil cells. In: Chen J, Wang Y, Duffy TS, Shen G, and Dobrzynetskaia LF (eds) *Advances in High-Pressure Technology for Geophysical Applications*, pp. 397–412. Amsterdam, The Netherlands: Elsevier B.V.

with the zero point in the spectrum corresponding to 14.4125 keV (Figure 16). From the NRIXS spectrum, the PDOS can be calculated (Sturhahn et al., 1995). An example of the PDOS is given in Figure 17 for Fe at three different temperatures and high pressure.

The low-frequency part of the PDOS is related to the Debye sound velocity (Hu et al., 2003):

$$\frac{3}{v_D^3} = \frac{1}{v_p^3} + \frac{2}{v_s^3} \quad [15]$$

Parabolic fits to the low-frequency portion of the PDOS give v_D . If the bulk modulus and density of the sample at high pressure are known, for example, through static compression experiments, then eqns [1], [2], and [15] allow one to solve for the aggregate sound velocities v_p and v_s . The Grüneisen parameter and thermal expansion must also be known to convert isothermal to adiabatic quantities. This method has been used to calculate the velocities of Fe at high pressure and temperatures (Lin et al., 2005a; Mao et al., 2001).

Further details on NRIXS, and its applications to samples of geophysical interest, can be found in the review articles by Sturhahn (2004) and Lin et al. (2005b).

2.12.5.2 IXS from Phonons

IXS by phonons is analogous to Brillouin scattering with x-ray instead of with visible light. The frequency of x-ray photons is changed due to interaction with thermally generated phonons

in a material. The two techniques differ in the methods of detecting the frequency shift (energy transfer) of the x-ray photons. Like Brillouin scattering, the IXS technique allows the measurement of sound velocities in single crystals and polycrystalline samples. A review of IXS is given by Burkel (2000), and its application to materials of geophysical interest and high-pressure research is given by Fiquet et al. (2004).

A main advantage of the IXS technique over visible light scattering methods, such as Brillouin scattering and ISS, is that x-rays penetrate all materials. This makes it possible to determine the body wave sound velocities (v_p and v_s) on optically opaque substances. One can therefore directly measure the elastic moduli and sound velocities of materials relevant to the Earth's core, such as Fe and its alloys (Fiquet et al., 2001, 2004). There are no refractive index effects.

A diagram of the IXS facility at beam line ID28 of the European Synchrotron Radiation Facility (ESRF) synchrotron is shown in Figure 18 to illustrate the measurement technique. In this experiment, the momentum transfer is chosen at desired values of $2|k_s|\sin(\theta/2)=q$, and the frequency of the input radiation is scanned to determine the energy transfer. Five analyzers are mounted 6.5 m from the sample on a Rowland arm that rotates in the scattering plane about a vertical axis through the sample, allowing one to access different values of θ , q . In this way, the phonon dispersion curves for each acoustic mode can be obtained and are usually fit with a sine function to obtain the velocities corresponding to the Brillouin zone center. The energy transfer at a chosen value of q is scanned by changing the temperature on the final backscattering Si monochromator. An example of the raw data, showing intensity of scattered x-rays as a function of the energy transfer of the input x-rays, is shown in Figure 19. From the velocities as a function of crystallographic direction, the elastic moduli can be obtained exactly as for the other single-crystal techniques described in the preceding text.

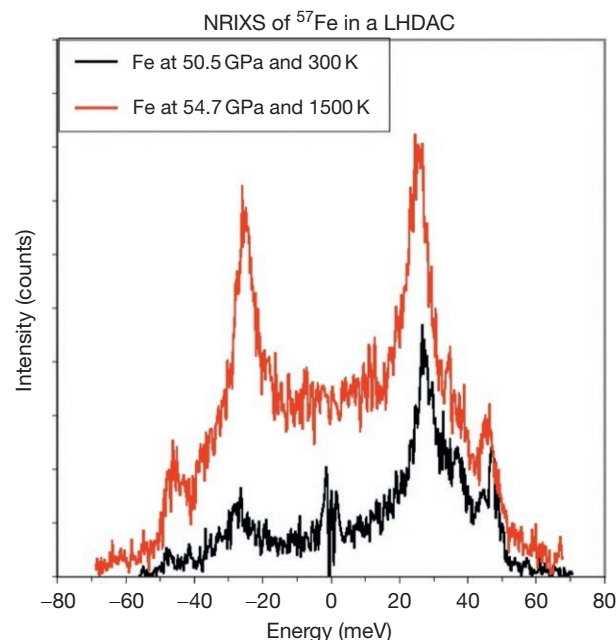


Figure 16 A nuclear-resonant inelastic scattering spectrum for ^{57}Fe . Zero energy corresponds to the 14.4125 keV nuclear transition energy of ^{57}Fe . Note the difference in intensity of Stokes and anti-Stokes peaks (symmetrically right and left of zero energy, respectively), which is an indicator of temperature. Reproduced from Lin JF, Sturhahn W, Zhao J, Shen G, Mao HK, and Hemley RJ (2004) Absolute temperature measurement in a laser-heated diamond anvil cell. *Geophysical Research Letters* 31: L14611. <http://dx.doi.org/10.1029/2004GL020599>.

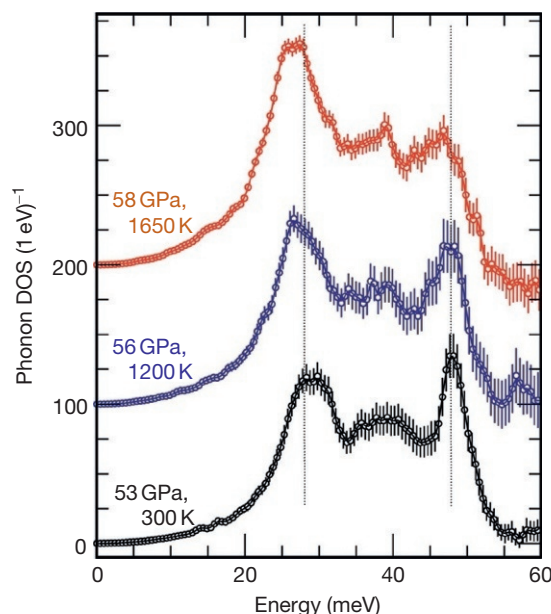


Figure 17 Phonon density of states of Fe at high pressure and temperatures, determined by NRIXS experiments in the diamond anvil cell. Courtesy of Jung-Fu Lin.

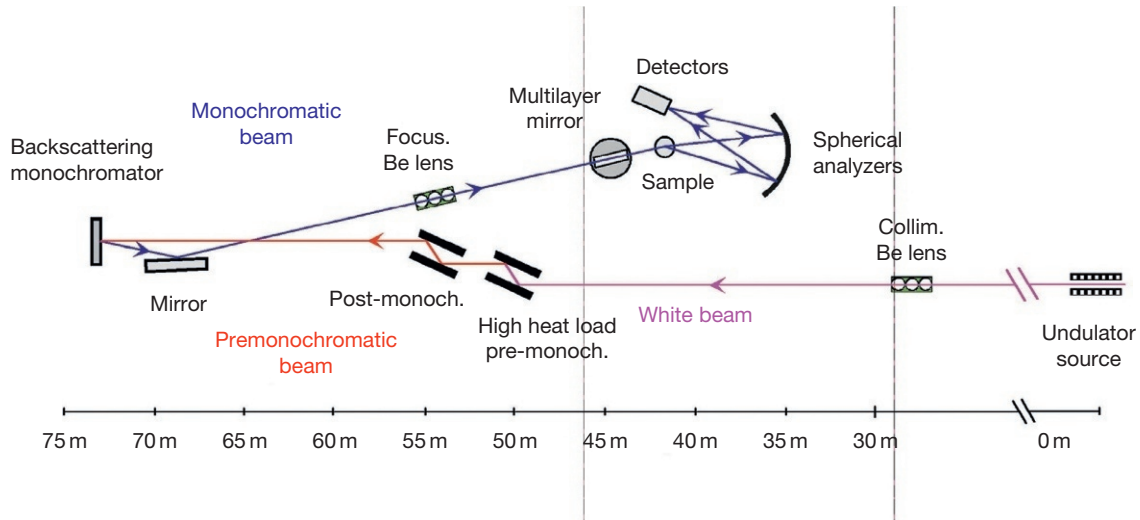


Figure 18 Momentum-resolved inelastic x-ray scattering setup at beam line ID-28 of the ESRF synchrotron in Grenoble, France.

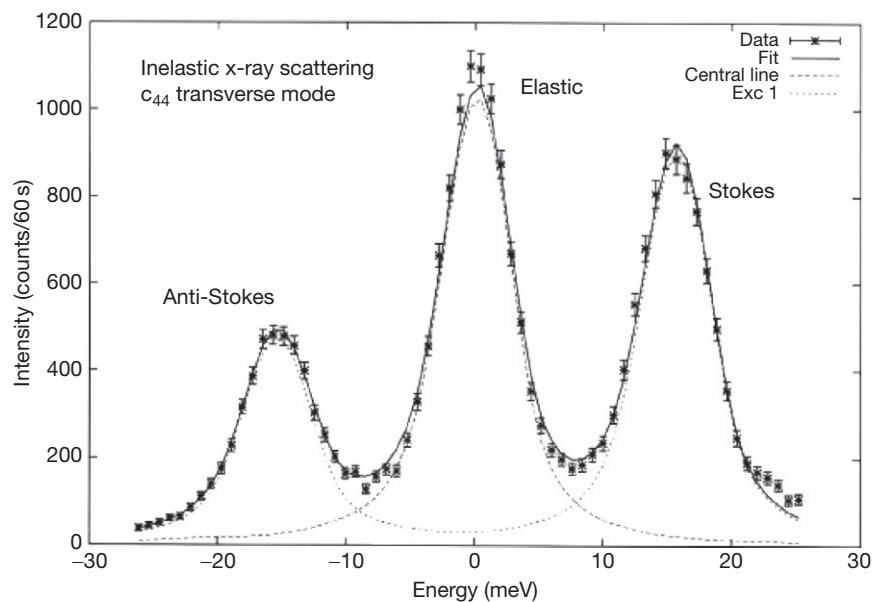


Figure 19 Inelastic x-ray scattering spectrum for Fe- and Al-bearing Mg silicate perovskite. The central peak at zero energy transfer is from elastic scattering. The peaks at $\sim \pm 15$ meV are scattering due to the pure shear mode c_{44} .

2.12.6 Shock Waves

Shock wave results on rocks and minerals have had a major influence on our understanding of the formation and evolution of planetary bodies. Dynamic shock compression studies allow one to access pressure and temperature regimes (hundreds of GPa and over 10 000 K) that are inaccessible to other techniques. Shock techniques have been developed to measure a wide variety of properties and processes, and a complete survey of this field cannot be presented here. Rather, we mention only the shock wave equation-of-state experiments that are the basis for much of what is inferred about the deeper parts of the Earth and other planets. Excellent reviews of shock wave theory and experimental methods are given by [Rice et al.](#)

(1958), Davison and [Graham](#) (1979), [Al'tshuler](#) (1965), [Duvall and Fowles](#) (1963), and [McQueen et al.](#) (1970).

In a shock wave experiment, a sample is impacted at high velocity by a flyer plate, producing a high density state that propagates through the sample with shock velocity U_s ([Figure 20](#)). The locus of all shock states that can be achieved by a sample in given initial state is known as the Hugoniot. The relationship between the Hugoniot and an isotherm or isentrope is shown in [Figure 20](#). It is important to realize that the temperature increases rapidly along the Hugoniot, and it is hotter than the isentrope (along which temperature increases adiabatically). Therefore, the pressure corresponding to a given compressed volume is higher along the Hugoniot. In a standard shock wave equation-of-state experiment, the pressure

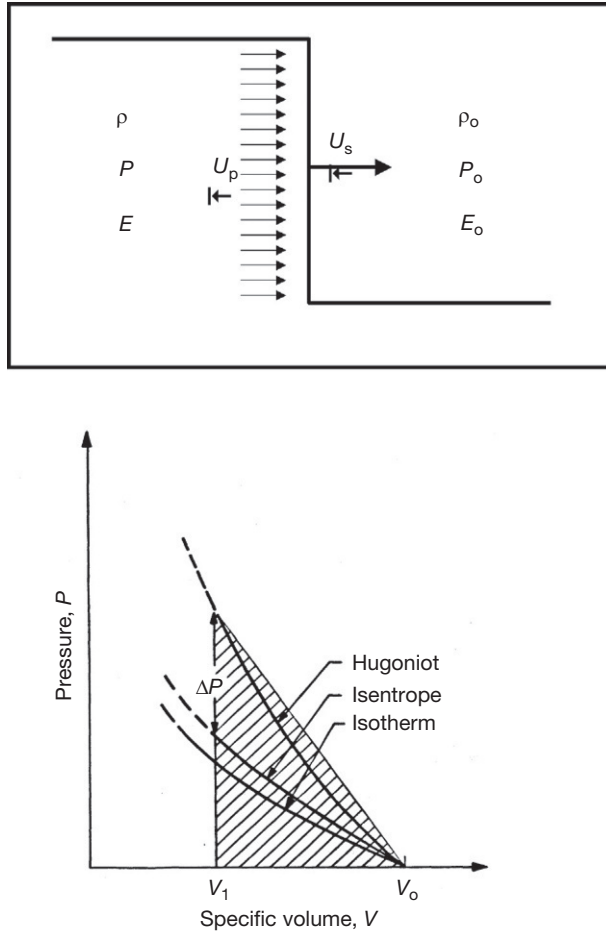


Figure 20 (Top) Schematic illustration of the states behind and in front of an advancing shock wave. (Bottom) The relationship of the Hugoniot to an isentrope and an isotherm.

and density (or specific volume) are determined, but the temperature is generally unknown. It is worth noting that the pressures in shock experiments are known with relatively high accuracy, on the order of 1%. This makes shock wave experiments important in the determination of pressure scales for high-pressure research.

From conservation of mass, momentum, and energy across the shock front, one obtains the Rankine–Hugoniot relations:

$$\begin{aligned} \rho_0 U_s &= \rho(U_s - u_p) \\ P - P_0 &= \rho_0 U_s u_p \\ E - E_0 &= (P + P_0)(V_0 - V)/2 \end{aligned} \quad [16]$$

where U_s and u_p are shock velocity and particle velocity, respectively, and P , V , and E are the pressure, volume, and internal energy in the shocked Hugoniot state, respectively. In a shock equation-of-state experiment, the shock velocity and particle velocity are measured. U_s is the transit time of the shock front through the sample. The particle velocity can be obtained by measuring the velocity of the impactor (flyer plate) through an impedance matching method (McQueen et al., 1970). With the knowledge of the initial pressure and density of the material, the density, pressure, and change in internal energy in the shocked state are thus known. It is empirically determined that

in the absence of phase changes, U_s and u_p form a linear trend, and the results of shock wave experiments are often represented in this way (Ahrens and Johnson, 1995).

The results of shock equation-of-state experiments have been critical to our understanding of the Earth's deep interior. For example, experiments on Fe provide compelling evidence that the density of the outer core is too low for it to be composed of pure Fe and therefore contains light elements. However, it should be recognized that many other types of sophisticated shock wave experiments are being performed, of which we will mention two. Hugoniot temperatures have been inferred by analysis of the thermal radiation emitted by shocked samples (Bass et al., 1990; Lyzenga and Ahrens, 1980). The measurements of sound velocities can be made along the Hugoniot and can provide evidence for phase transitions that are not readily apparent by other types of data (Brown and McQueen, 1986; Nguyen and Holmes, 2004). New technologies such as the ability to produce shock waves by laser ablation may open up yet further opportunities to investigate the properties of deep Earth materials (Swift et al., 2004).

2.12.7 Other Techniques

Elasticity measurements have a long history due to their importance in many areas of physics, chemistry, and materials sciences. This chapter is not exhaustive, and a number of measurement techniques have necessarily not been discussed. Perhaps most noteworthy is inelastic neutron scattering, which is arguably the optimal way to investigate phonons (e.g., Shirane, 1974). This method has found limited applications in geophysics, because of the large sample size requirements for neutron studies. However, significant progress is being made in the use of neutron scattering for investigations at high pressures (Besson et al., 1992). Another technique that has been used to provide constraints on the strength and elasticity of materials is radial XRD in the DAC (e.g., Merkel et al., 2002; Speziale et al., 2006).

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2.13 Measuring High-Pressure Electronic and Magnetic Properties

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Glossary

Bonding in deep Earth materials Description of the binding between atoms and molecules in substances that comprise the interior of the planet, typically the mantle and core.

Bonding under high P - T conditions Description of the binding between atoms and molecules at high pressures and temperatures such as those that characterize the Earth and other planets.

Brillouin and Rayleigh scattering Inelastic light-scattering technique in which light is scattered off areas of altered density caused by acoustic waves in a material.

Charge transfer Excitations or bonding states derived by promotion of an electron from one atom or molecule to another atom or molecule.

Compton scattering (CS) Inelastic scattering of x-ray radiation typically used to probe electron momentum distributions.

Conventional bonding classification The description of binding forces in atoms and molecules found in gases, solids, and liquids under ambient or near-ambient conditions, specifically covalent, ionic, metallic, van der Waals, and hydrogen-bonding.

Crystal field transitions Excitations between quantum states of an atom, ion, and molecule inside a crystal where the states are perturbed (e.g., degeneracies lifted) by the symmetry of the site of the crystal.

de Haas-van Alphen Technique for measuring Fermi surfaces of metals in a magnetic field.

Defect excitations Transitions or spectral features arising from defects in the material, including color centers.

Dielectric functions The response of a material to an applied electric field.

Elastic neutron scattering Scattering of neutron without a change in particle energy, as in typical neutron diffraction.

Elastic x-ray scattering Scattering of x-rays without changes in photon energy as in typical x-ray diffraction, may be either coherent or incoherent.

Electrical conductivity Movement of charge in a system in response to an applied electric field (static or frequency-dependent) and can be intrinsic or extrinsic, electronic or ionic.

Electron paramagnetic resonance (EPR) Technique that involves resonant microwave absorption between electronic energy levels split in a magnetic field (the Zeeman effect).

Electronic inelastic x-ray scattering (EIXS) Technique to probe electronic excitations such as core level, plasmons,

and electronic bands, using x-rays, including momentum q dependence.

Electronic structure Quantum description of electrons in an atom, molecule, or condensed phase (i.e., crystal, liquid, fluid, or glass).

Excitons Well-defined quantum excitations or quasi-particles such as bound electron-hole pairs in crystals.

Extended excitations Spectral transitions that involve electronic states that are coherent over long distances, as in a metal.

High P - T CARS Coherent anti-Stokes Raman scattering, a nonlinear optical technique whereby a pump beam ω_p and a Stokes beam ω_s are mixed via third-order susceptibility, typically used to study vibrational transitions.

Inelastic x-ray scattering spectroscopy (IXSS) General class of techniques that measure excitation spectra, probes the dynamical structure factor.

Infrared spectroscopy Class of techniques that use radiation from 10 to 10 000 cm^{-1} in absorption, emission, or reflectivity and used to study vibrational, electronic, and magnetic excitations.

Iron and iron alloys Soft, silver-colored metal with an atomic number of 26; the most abundant transition element in the solar system; iron alloys are a mixture of iron and other elements.

Kramers-Kronig analysis Mathematical treatment that uses causality to determine the full set of optical constants of a material as a function of frequency to its complete spectrum (e.g., absorption and reflectivity).

Luminescence Light emitted by materials; includes both fluorescence (short-lived) and phosphorescence (long-lived).

Magnetic excitations Transitions between magnetic states in materials, such as magnons.

Magnetic properties Properties arising from the presence of unpaired electrons and giving rise to a magnetic field or the response of a material to an external magnetic field.

Nonlinear optical methods Optical techniques in which the response of the material under study involves the nonlinear response (susceptibility) or, in other words, more than photon.

Nuclear magnetic resonance (NMR) Technique that uses radio-frequency radiation to probe transitions associated with nuclei that split in a magnetic field.

Nuclear resonance forward scattering (NRFS) Time-domain technique that uses synchrotron radiation to probe the Mössbauer effect in materials.

Nuclear resonant inelastic x-ray scattering

(NRIXS) Synchrotron radiation technique that probes phonon spectra associated with the excitation of the Mössbauer-active nuclei.

Olivine $(\text{Mg,Fe})_2\text{SiO}_4$; is a magnesium iron silicate, one of the most common minerals in the Earth's upper mantle.

Optical absorption and reflectivity Techniques used to study transitions in the infrared–visible–ultraviolet spectral range from transmission of light through the material (absorption) or from the light reflected from the surface.

Oscillator fits Analyses of spectra that employ one or more excitations to comprise the spectra profile, often used for modeling dielectric function.

Phonon inelastic x-ray scattering (PIXS) Technique to probe vibrational excitations, including their momentum q dependence, using x-rays.

Raman scattering Inelastic light-scattering technique that measures transitions to an excited state from the ground state (Stokes scattering) and to the ground state from a thermally excited state (anti-Stokes scattering).

Rayleigh scattering Quasi-elastic scattering spectroscopy technique, typically used to explore relaxation phenomena in materials.

Resonance methods Techniques that probe materials by measuring the response through a characteristic frequency or frequencies.

Resonant inelastic x-ray spectroscopy (RIXS) Technique to probe electronic excitations using x-rays scattered at energies that are different from the incident x-rays and where the incident radiation is tuned through core-level excitations.

Silicate perovskite and postperovskite High-pressure silicate phases with the stoichiometry ASiO_3 , where A is a

metal ion (e.g., Mg, Fe, and Ca). Silicate perovskite represents the dominant class of phase of the Earth's lower mantle.

Silicate postperovskite Dense pressure phase of the same stoichiometry as silicate perovskite having the CaIO_3 structure and stable at P – T conditions of the base of the mantle.

Transition metal oxides Compounds with the general formula $\text{M}_a^i\text{M}_b^j\text{O}_z$, where M_a^i is a transition metal in a particular oxidation and O is oxygen.

Transport measurements Experiments that quantify the transport of charge (electrons, protons, or ions) and of heat (thermal conductivity).

Volatiles Low boiling point compounds usually associated with a planet's atmosphere or crust, including hydrogen, H_2O , CO_2 , methane, and ammonia; also the components of these materials that can be bound in high-pressure phases.

x-Ray absorption spectroscopy (XAS) Technique in which incident x-rays are absorbed when energy exceeds the excitation energy of core electrons of a specific element, typically causing an atomic edge-like spectrum.

x-Ray emission spectroscopy (XES) Technique in which core electrons are excited by x-ray and then the core holes decay through a radiative process.

x-Ray inelastic near-edge spectroscopy (XINES) Technique in which an incident x-ray is scattered at a lower energy of a core excitation (e.g., K -edge) of a material; typically used to probe structure containing information on bonding states.

x-Ray magnetic circular dichroism (XMCD) Technique to measure the spin polarization of an electronic excitation of materials by the use of circularly polarized x-rays.

Abbreviations

CS	Compton scattering	NRIXS	Nuclear resonant inelastic x-ray scattering
EIXS	Electronic inelastic x-ray scattering	PIXS	Phonon inelastic x-ray scattering
EPR	Electron paramagnetic resonance	RIXS	Resonant inelastic x-ray spectroscopy
IXSS	Inelastic x-ray scattering spectroscopy	XAS	x-Ray absorption spectroscopy
NMR	Nuclear magnetic resonance	XES	x-Ray emission spectroscopy
NRFS	Nuclear resonance forward scattering	XINES	x-Ray inelastic near-edge spectroscopy
		XMCD	x-Ray magnetic circular dichroism

2.13.1 Introduction

Electronic and magnetic properties directly influence large-scale global phenomena ranging from the initial differentiation of the planet, the formation and transmission of the Earth's magnetic field, the propagation of seismic waves, to the upwelling and downwelling of mass through the mantle. The properties of deep Earth materials are not readily familiar to us, owing to their distance, both physically and conceptually, from the near-surface environment of the planet. Over the range of pressures encountered with the Earth, rock-forming oxides and silicates compress by factors of two to three. Even

the many incompressible materials are compressed by 50%. Volatiles such as rare gases and molecular species can be compressed by over an order of magnitude. With the large reduction in interatomic distances produced by these conditions, dramatic alterations of electronic and magnetic properties give rise to myriad transformations. Discrete electronic and magnetic transformations can occur, such as metallization of insulators and magnetic collapse. More commonly, these changes are associated with, and drive, other transformations such as structural phase transitions, as well as controlling chemical reactions. Materials considered volatiles under near-surface conditions can be structurally bound in dense,

high-pressure phases (e.g., hydrogen in ice, mantle silicates, and ferrous alloys). Gases and H_2O become refractory (high melting-point) materials at high pressures (Lin et al., 2005a). The heavy rare gases metallize (Eremets et al., 2000; Goettel et al., 1989; Reichlin et al., 1989). Ions such as Fe^{2+} and Mg^{2+} , which almost always can substitute completely for each other at low pressures, partition into separate phases at depth (Mao et al., 1997), whereas incompatible elements such as Fe and K may form alloys (Parker and Badding, 1996). Noble gases form new classes of compounds (Sanloup et al., 2002b; Vos et al., 1992).

This chapter constitutes an overview of measurements of high-pressure electronic and magnetic properties of Earth materials. The chapter draws largely on a pedagogical review written in 1998 (Hemley et al., 1998b), including numerous updates as a result of considerable advances in the field, particularly in the area of synchrotron techniques. The article focuses on in situ high P - T techniques and selected applications in geophysics. We begin with a short review of fundamental properties, with emphasis on how these are altered under very high pressures and temperatures of the Earth's deep interior. This is followed by a discussion of different classes of electronic and magnetic excitations. We then provide a short description of various techniques that are currently used for high-pressure studies. We then selected examples, showing how the use of a combination of different techniques reveals insight into high P - T phenomena.

2.13.2 Overview of Fundamentals

2.13.2.1 Bonding in Deep Earth Materials

2.13.2.1.1 Conventional bonding classification

The binding forces that hold the atoms together are generally electrostatic in origin. The forces that keep the atoms from collapsing into each other arise from increased kinetic energy as atoms are brought closer together, the Pauli exclusion principle that keeps electrons apart, the electrostatic repulsion between electrons, and ultimately, as the atoms are brought closer and closer together, the electrostatic repulsion of the nuclei. Crystals can be characterized by the primary source of their binding energy. Following the conventional classifications set out by Pauling (1960), we describe for the purposes of the present chapter the following bonding types: ionic, covalent, metallic, van der Waals, and hydrogen bonding. As pressures increase, the problem changes from understanding the cohesion of crystals to understanding how electronics and nuclei rearrange in order to minimize repulsive forces.

In ionic crystals, the primary source of binding is from the electrostatic attraction among ions. Prototypical examples are NaCl (Na^+Cl^-) and MgO ($\text{Mg}^{2+}\text{O}^{2-}$). This ionicity is driven by the increased stability of an ion when it has a filled shell of electrons. For example, oxygen has a nuclear charge $Z=8$, which means that it would have two 1s, two 2s, and four 2p electrons, but a filled p shell has six electrons. In a covalent bond, charge concentrates in the bonding region, increasing the potential and kinetic energy of interaction between electrons but reducing the energy through the electron-nuclear interactions (since each electron is now on average close to both nuclei). Covalent bonds tend to be directional since they

are formed from linear combinations of directional orbitals on the two atoms. It is straightforward to develop models for such covalent materials, and such models have ranged from models with empirical parameters to those with parameters obtained from first principles. The high-pressure behavior of metals, and in particular iron and iron alloys, is of paramount importance for understanding the nature of the Earth's core. The bonding in metals is often thought of as a positive ion core embedded in a sea of electrons, the negative electrons holding the ions together. Under pressure, the conductivity may increase or decrease: in some cases (e.g., carbon) pressure may drive a transition from a metallic phase (graphite) to an insulator (diamond).

One must also consider weaker bonding interactions. Dispersion, or van der Waals forces, arises from fluctuating dipoles on separated atoms or molecules. Separated, nonoverlapping charge densities have such an attractive force between them, and it varies as $1/r^6$ and higher-order terms at large distances. Even at low pressures, van der Waals forces are largely quenched in solids and become completely insignificant at high pressures. Hydrogen bonds are essentially ionic bonds involving H and O; a hydrogen atom is covalently bonded to an oxygen atom and attracted electrostatically to a neighboring oxygen ion. As such, the three atoms form a linear linkage with a hydrogen atom asymmetrically disposed between the oxygens, a configuration that is ubiquitous in hydrous materials. A range of degrees of hydrogen bonding at ambient pressure are evident in dense hydrous silicates that are candidate mantle phases. In such structures, the application of moderate pressures causes a reduction in oxygen-oxygen distances, which generally enhances bonding between the hydrogen and the more distant oxygen atom. At deep mantle and core pressures, conventional hydrogen bonding is lost, and hydrogens might be symmetrically situated between oxygens.

Many high-pressure minerals exhibit combinations of the types of interactions outlined in the preceding text. The most common are ionic bonding and covalent bonding, both within the same bond and different degrees of each in different bonds present in the material. Silicates are considered about half-ionic and half-covalent. Transition metals such as Fe are both metallic and covalent. A molecular group that contains strong covalent bonds can also be ionically bound to other ions in the crystal. An example is CaCO_3 , where the C-O bonds are strong and directional, forming a planar triangle in the CO_3^{2-} carbonate group, which is bound ionically to Ca^{2+} ions.

2.13.2.1.2 Bonding under high P - T conditions

The bonding in Earth materials characterized under ambient conditions typically does not reflect their state under conditions of the deep Earth. The contributions from each type are in general strongly pressure-dependent. High pressure favors high density and high temperatures favor phases with higher entropy S . At lower mantle and core conditions, the density terms dominate, with generally small Clapeyron slopes, dP/dT , found for solid for phase transitions. Structures tend to adopt more close-packed configurations with increasing compression. At high pressures, the attractive terms in molecular solids become less and less important, and one could rather think of the atoms as soft spheres. Much of the chemistry and phase

diagrams of such materials can be understood as the packing of spheres of various sizes. However, as pressure is increased, the electronic structure also changes. This happens first in the crystals of heavier rare gases such as Xe, which transforms from the fcc to the hcp structure (Jephcoat et al., 1987) prior to metallization (Eremets et al., 2000; Goettel et al., 1989; Reichlin et al., 1989). On the other hand, the tendency toward close packing is not observed in all cases. There have been a few theoretical treatments of these phenomena (Neaton and Ashcroft, 1999, 2001). In fact, surprisingly complex structures can be adopted, as has been seen in some pure elements (McMahon and Nemes, 2004). Oxides can also adopt complex structures, driven by subtle pressure-induced changes in orbital hybridization. This is particularly evident in some ferroelectric materials (Wu and Cohen, 2005). In addition, there can be effects of magnetism, or the tendency of electron spins to align: theory and a number of experiments indicate that magnetism tends to decrease and disappear with increasing pressure (Cohen and Mukherjee, 2004; Cohen et al., 2002; Pasternak and Taylor, 2001; Pasternak et al., 1997b; Steinle-Neumann et al., 2003, 2004a,b; Stixrude, 2001).

Changes in bonding also apply to liquids. For the deep Earth, the important systems are silicate and oxide melts and liquid iron alloys of the outer core. There is evidence that silicate melts undergo similar structural transformations such as coordination changes, although not abrupt, and spread out over a range of pressures. Detailed information on the electronic properties of geophysically relevant liquids under extreme conditions is lacking. Insulating materials can also become metallic at high temperatures and pressures, as has been observed and computed in FeO (Ohta et al., 2012).

2.13.2.2 Electronic Structure

Insight into these phenomena must come from examination of the changes in electronic structure induced by materials subjected to extreme P - T conditions. Because of the presence of long-range interactions in condensed phases, the bonding must in general be viewed from an extended point of view, although a local picture is often employed to simplify the problem. For crystals, the eigenstates can be characterized by the wave number k (Kittel, 1996). The interaction between orbitals on different atoms gives rise to energy bands, which are dispersive as functions of k , and the band energies versus k form the band structure. The core states, or deep levels for each atom, remain sharp delta function-like states, which may be raised or lowered in energy relative to their positions in isolated atoms. These core-level shifts are due largely to the screened Coulomb potential from the rest of the atoms in the crystal. The occupied valence and empty conduction states no longer look like atomic states, but are broadened into energy bands. There are often intermediate states between the core levels and the valence states called semicore states that are slightly broadened at low pressures but that become broader and more different from atomic states with increasing pressure. The formation of ions is driven by the increased stability of an ion when it has a filled shell of electrons. The strong attractive electrostatic, or Madelung, interaction between the ions greatly enhances the crystal stability.

This picture now becomes a means for classifying different materials. Metals have partially occupied states at the Fermi level, the highest occupied energy level in a crystal. One can understand the insulating behavior of materials with fully filled bands by considering what happens when one applies an electric field. An electric field raises the potential at one part of the sample relative to another, and one would think that electrons would then flow down that potential gradient. However, in an insulator, the bands are filled, and due to the Pauli exclusion principle, nothing can happen without exciting electrons to states above the gap. This requires a large energy, so there is no current flow for small fields, and thus, the materials have a finite susceptibility and the material is insulating. In a metal, the partially filled states at the Fermi level mean that current will flow for any applied field, and the susceptibility is infinite. Actually, the distinction between metallic and insulating systems involves some subtle physics (Resta, 2002), but in general, the band picture suffices to understand metals and insulators well within their stability fields. Insulator to metal transitions, however, are expected to show complex behavior in some materials (Huscroft et al., 1999). Many transitions found to date seem to involve structural transitions at the same pressure as the metal-insulator transition (e.g., FeO from the rhombohedrally strained rock salt structure to the anti-B8 (inverse NiAs) structure) (Fei, 1996; Gramsch et al., 2003; Mazin et al., 1998; Murakami et al., 2004b), but an isostructural transition has been seen in MnO (Yoo et al., 2005) and FeO (Ohta et al., 2012).

In an insulator, the energy of the highest occupied levels is the valence band, designated E_v , and that at the bottom of the conduction band, E_c . The difference is the bandgap, $E_g = E_c - E_v$. Crystals with bandgaps between occupied and unoccupied states should be insulators, and those with partially filled bands should be metals. Localized states may exist at energies between the valence and conduction bands, and these can have major effects on optical and transport properties. If the gap is small or if the material has such intermediate states (e.g., by chemical doping such that electrons can be excited into the conduction bands or holes in the valence bands), the crystal is considered a semiconductor. In a nonmagnetic system, each band holds two electrons, and thus, a crystal with an odd number of electrons in the unit cell should be a metal since it will have at least one partially filled band. Magnetic crystals that are insulators by virtue of local magnetic moments are known as Mott insulators (Mott, 1990). These materials include transition metal-containing oxides present in the mantle (and considered core components); such materials exhibit intriguing behavior as a function of pressure and temperature.

We should also consider the electronic structure of non-crystalline materials, including liquids. The existence of a bandgap in crystals can be described in terms of the Brillouin zone and Bragg-like reflection of electrons. But a gap does not depend upon the periodicity of the atoms on a lattice. The electrons in the lowest energy states in the conduction band of a noncrystalline material (or disordered crystal) can be localized (Anderson, 1958; Mott, 1990). The difference between the localized and delocalized states is called the mobility edge. These may be important in describing the electronic properties of liquids and amorphous materials formed from deep Earth crystalline materials (e.g., metastably compressed crystalline minerals and dense melts).

2.13.2.3 Magnetic Properties

Magnetism arises from the presence of unpaired electrons. Electrons have magnetic moments, but if they are paired up in states as up and down pairs, there will be no net magnetism in the absence of a magnetic field. However, in open-shelled atoms, there may be a net moment. According to Hund's rules, atoms (or isolated ions) will maximize their net magnetic moment, which lowers their total energy due to a decrease in electrostatic energy. In a crystal, interactions with other atoms and formation of energy bands (hybrid crystalline electronic states) may lead to intermediate- or low-spin magnetic structures.

The behavior of iron (Fe^{3+} , Fe^{2+} , and Fe^0) at high pressure is of central importance. Fe^{2+} has six d-electrons, and two end-member situations can be considered. In a site with octahedral symmetry and limited ligand-field interactions, the six d-electrons can be paired to fill three t_{2g} states, forming low-spin, ferrous iron, and there is no net magnetic moment. In high-spin ferrous iron, five up d-states are split in energy from five down d-states by the exchange energy, and five d-electrons go into the three t_{2g} and two e_g lower-energy, majority spin states and one electron into a high-energy t_{2g} state. This gives a net magnetic moment component of $4\mu_B$ (Bohr magnetons). The fully spin-polarized magnetic moment component of Fe^{3+} is $5\mu_B$. In crystals, the 4s states usually dip down in energy with respect to k and are partially occupied, leading to a smaller d-occupation and smaller net moment.

Such open-shell systems have often been discussed in terms of crystal field theory, which has been very successful in rationalizing optical spectra, crystal chemistry, and thermodynamic and magnetic properties of minerals, including their pressure dependencies. The principal assumption of crystal field theory is the existence of localized atomic-like d-orbitals. It has provided a way to rationalize the changes in energy levels in terms of local interactions of the transition metal cations with the coordinating atoms. The symmetry of the coordination polyhedron results in a lifting of the otherwise degenerate d-orbitals. The primary success of crystal field theory arose from symmetry analysis of the splitting of the atomic-like states. These symmetry arguments are rigorous, but the origin of the splitting may not arise from a potential field represented as a point charge lattice, but rather to bonding hybridization. Furthermore, d-states are not pure atomic-like states but are dispersed across the Brillouin zone (energy varies with k).

As shown by Mattheiss (1972), the origin of the crystal field splitting is due largely to hybridization. In the language of quantum mechanics, the $e_g - t_{2g}$ splitting is due to off-diagonal interactions, not shifts in the diagonal elements as would be the case for the conventional electrostatic crystal field interaction. The splitting can be considered a ligand-field effect and does not arise from changes in the electrostatic field at an atomic site. Rather, the splitting is due to d-d interactions between next-nearest neighbors and due to p-d and s-d interactions between neighboring oxygen ions. The d-d interactions led to splittings that vary as $1/r^5$; although the p-d and s-d interactions follow a $1/r^7$ dependence (Harrison, 1980), the metal-metal d-d splittings dominate. Thus, the same $1/r^5$ dependence of the observed splittings is predicted by electrostatic crystal field model (Drickamer and Frank, 1973) and by hybridization (Mattheiss, 1972).

In the low-temperature ground states, moments on individual ions or atoms can be oriented, giving rise to ferromagnetism if they are lined up in the same direction or antiferromagnetism if they are oppositely aligned, which depends on the sign of the magnetic coupling J , which depends on hybridization with other atoms in the crystal. At high temperatures, the moments will disorder, but there are still local moments present. This paramagnetic state is distinguished from the paramagnetic state that arises from loss of local moments (magnetic collapse or a high- to low-spin transition), although the two states merge continuously into each other with increasing pressure. Ferrimagnetism results when the magnetic moments are unequally distributed over different sublattices. A net spontaneous magnetic moment arises from the incomplete cancellation of aligned spins. An example is magnetite, Fe_3O_4 , which consists of a sublattice of Fe^{2+} and one of Fe^{3+} . In some materials, such as fcc and possibly iron (Cohen and Mukherjee, 2004), the moments are non-collinear. For ferromagnetic (FM) and antiferromagnetic (AFM) phases, the magnetic moments are aligned below the Curie and Néel temperatures, respectively. The decrease in magnetism with pressure can be understood qualitatively from the increase in electronic bandwidths, which eventually become greater than the exchange splitting. This can be understood more quantitatively with the Stoner and extended Stoner models (Cohen et al., 1997).

2.13.3 Electronic and Magnetic Excitations

Excitations in a system are induced by external (e.g., electronic or magnetic) or internal (e.g., temperature) fields. The coupling of the response to the field is given by the frequency-dependent susceptibility. This can be characterized as the dielectric function $\epsilon(\omega, k)$, where ω is the frequency and k is the wavevector (the dielectric function is also known as the relative permittivity). The dielectric function is complex, $\epsilon = \epsilon_1 + i\epsilon_2$, where ϵ_2 contains the contribution from absorption. In general, the response of a crystal to an electric field is dependent on its orientation relative to the crystal axes (which gives rise to properties such as birefringence and optical activity), that is, the dielectric function is a tensorial function). The dielectric tensor is also a function of applied electric field, giving rise to nonlinear optical response (e.g., multiphoton excitations) as described later in the text. Electrons can be excited into extended or itinerant states (i.e., across the band-gap), or the excitations may be local (i.e., forming a localized electron-hole pair, or exciton).

2.13.3.1 Dielectric Functions

The index of refraction is related to the dielectric function ϵ , as $n^2 = \epsilon$, which can strongly depend on pressure. In general, there are several different contributions to the dielectric function. In materials that contain polar molecules, the molecules can align. There are three main contributions to the dielectric response in insulators: ionic polarization (displacement of ions) in crystals containing nonpolar atoms or ions, electronic polarization (from the deformation of atomic charge distributions), and charge transfer from atom to atom. The electronic

contribution to the dielectric function of a material is formally determined by the sum of its electronic excitations (Ashcroft and Mermin, 1976). Hence, measurement of the index of refraction of transparent minerals (i.e., below bandgap or absorption edge) can be used to constrain the frequency of higher-energy electronic excitations (e.g., in the ultraviolet spectrum), for example (Eremets, 1996). Optical spectra of oxides and silicates from the near-IR to the vacuum UV are determined by electronic transitions involving the valence (bonding) band, the conduction (antibonding) band, and d-electron levels. Piezoelectric crystals become polarized when subjected to a mechanical stress (compressive or tensile). Quartz is a common example. In ferroelectric phases, the crystals are spontaneously polarized and have very high dielectric constants.

This approach has been useful in high-pressure studies when the window of the high-pressure cell precludes measurements above a critical photon energy (Hemley et al., 1991). For example, diamond anvil cells at zero pressure have an intrinsic absorption threshold of 5.2 eV (i.e., for pure type IIa diamonds). Moreover, type I diamonds contain nitrogen impurities that lower the effective threshold at zero pressure to below 4 eV (depending on the impurities). Although the bandgap of diamond increases under pressure, the absorption threshold of diamond (and most likely the gap) decreases in energy under the stresses due to loading in the cell. Full quantitative information on the dielectric function in the diamond transparency window is hard to obtain, although there exist few applications facilitating data analysis. Two mostly used approaches are oscillator model and the Kramers–Kronig (KK) analysis of the reflectivity data. Several experimental setups have been reported for reflectivity measurements (Goncharov et al., 2000; Syassen and Sonneschein, 1982); however, only relatively few studies have been performed that yield full dielectric function information under pressure (e.g., Goncharov et al., 1996).

The electronic dielectric function including intra- and inter-band electronic transitions can be computed from first principles within the random phase approximation using, for example, the WIEN2k LAPW code (Ambrosch-Draxl and Sofo, 2006; Schwarz et al., 2002). Predictions for high-pressure hydrogen (Cohen et al., 2013) will be useful for better understanding experimental spectroscopy. These calculations have been used to discriminate solid CO₂ phases (Sharma et al., 2003).

2.13.3.1.1 Oscillator fits

Classical oscillator fits are based on the following expression for the dielectric constant:

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) = \varepsilon_\infty + \sum_{j=1}^m \frac{\omega_{pj}^2}{\omega_j^2 - \omega^2 - i\omega\gamma_j} \quad [1]$$

where ω_j and γ_j are the frequency and line width, respectively, of oscillator j . The real and imaginary parts of the refractive index (omitting the ω dependence) $N = n + ik$ are related to the dielectric constant by

$$n = \left(\frac{(\varepsilon_1^2 + \varepsilon_2^2)^{1/2} - \varepsilon_1}{2} \right)^{1/2} \quad [2]$$

$$k = \left(\frac{(\varepsilon_1^2 + \varepsilon_2^2)^{1/2} + \varepsilon_1}{2} \right)^{1/2} \quad [3]$$

The following discussion is restricted to the analysis of the normal incidence of light at a sample–diamond interface, which is a good approximation to many experimental conditions. The reflectivity from the sample between diamond anvil cells having a thickness D is given in this case by the following equation, which is equivalent to the formula from Born and Wolf (1980), the only difference being written in complex numbers:

$$R = \left| \frac{(N - N_D)^2(1 - \chi)}{(N + N_D)^2 - \chi(N - N_D)^2} \right|^2 \quad [4]$$

where N_D is the refractive index of diamond and

$$\chi = \exp(i2N\omega D) = \exp(i2n\omega D - 2k\omega D) \quad [5]$$

For the case of a strong absorption a sample when the reflectivity from the second sample–diamond interface is negligible, one obtains well-known expression

$$R = |r|^2 = \left| \frac{(N - N_D)}{(N + N_D)} \right|^2 = \frac{(n - N_D)^2 + k^2}{(n + N_D)^2 + k^2} \quad [6]$$

2.13.3.1.2 KK analysis

In general, the response function r (eqn [6]) can be determined from the reflectivity R using the KK procedure (Bassani and Altarelli, 1983). One defines

$$\theta(\omega) = -\frac{2\omega}{\pi} P \int_0^\infty d\omega' \frac{\ln|r(\omega')|}{\omega'^2 - \omega^2} \quad [7]$$

where P is the principal part of the integral. From eqns [5] and [7], it is straightforward to calculate

$$n = \frac{N_D(1 - R)}{1 + R - 2\sqrt{R}\cos(\theta)} \quad [8]$$

$$k = \frac{2N_D(1 - R)\sin(\theta)}{1 + R - 2\sqrt{R}\cos(\theta)} \quad [9]$$

The dielectric constants are given then by

$$\varepsilon_1 = n^2 - k^2 \quad [10]$$

$$\varepsilon_2 = 2nk \quad [11]$$

This procedure works only in the region of strong absorption, where we can use eqn [4] instead of eqn [3]. Although all weak IR bands can often be observed in absorption, it is much more convenient to use Fourier transform techniques to carry out the KK transformation, instead of directly using eqn [7]. The following discussion is based upon the technique outlined in Titchmarsh (1937). The KK transformation is a transformation between the functions connected in the following way (Bassani and Altarelli, 1983):

$$f(x) = -\frac{1}{\pi} P \int_{-\infty}^\infty \frac{g(t)}{t - x} dt, \quad g(x) = \frac{1}{\pi} P \int_{-\infty}^\infty \frac{f(t)}{t - x} dt \quad [12]$$

For the present case, $g(x)$ and $f(x)$ can correspond to dielectric functions $\varepsilon_1(\infty) - \varepsilon_\infty$ and $\varepsilon_2(\omega)$. When calculating the phase of the reflectivity, the matching pair would be

$\ln |r(\omega)|$ and $\theta(\omega)$. Functions $g(x)$ and $f(x)$ are called Hilbert transforms, and their Fourier transforms $F(t)$ and $G(t)$ are coupled by the following relation (Titchmarsh, 1937):

$$G(t) = -iF(t)\text{sgn}(t) \quad [13]$$

where $\text{sgn}(x) = 0$ when $x < 0$ and $\text{sgn}(x) = 1$ when $x \geq 0$. Thus, taking the Fourier transform of $g(x)$ ($G(t)$), we can find the transform of $f(x)$ ($F(t)$) using eqn [13]; the inverse transform of $F(t)$ gives $f(x)$, thereby giving the KK transform of the function $g(x)$. Fast Fourier transform techniques permit the calculation of KK transforms easily and much faster than direct integration of eqn [7]. Formally, the transform should be performed over the frequency range $0 < \omega < \infty$, but experimental data are always limited to a specific frequency range. Procedures are therefore needed to account for missing data, and these procedures will be discussed later in the experimental section. When calculating the KK transform of $\ln |r(\omega)|$ at sample-diamond interface, there may be an additional contribution to the calculated phase shift, which is known as the Blaschke product (Stern, 1963). The phase shift is given by

$$\theta(\omega) = \theta_c(\omega) + \zeta(\omega) \quad [14]$$

where

$$\zeta(\omega) = -i \ln[B(\omega)] = 2 \sum_n \tan^{-1}[(\omega - \mu_n^r)/\mu_n^i] \quad [15]$$

Here, the summation runs over all n ; r and i stand for the real and imaginary parts of μ_n , and μ_n^r and μ_n^i are determined from the condition

$$r(\mu_n) = 0, \quad (\mu_n^r + i\mu_n^i = \mu_n) \quad [16]$$

$\theta_c(\omega)$ is a canonical phase shift that results from the KK procedure. The physical reason for the occurrence of the Blaschke product $\zeta(\omega)$ is a zero in reflectivity $r(\omega)$ in the upper half of the complex ω plane (eqn [16]), which introduces a singular point in $\ln |r(\omega)|$ and makes the application of the KK relation unjustified in that case. However, one can define the canonical reflectivity

$$r_c(\omega) = r(\omega)/[(\omega - \mu_n)(-\omega + \mu_n^*)] \quad [17]$$

which does not have zeros in the upper half of the complex ω plane. Moreover, on the real ω_r axis, $r(\omega_r) = r_c(\omega_r)$. Thus, the KK relation can be applied to the canonical reflectivity, and the resulting formula for the phase shift will be given exactly by eqn [14]. The Blaschke root μ_n is pure imaginary in this case ($\mu_n^r = 0$), because eqn [16] is satisfied when $n(\omega) + ik(\omega) - N_D = 0$ is fulfilled (which requires $k = 0$). It is known that the refractive index $N(\omega)$ is a complex number everywhere, except on the imaginary ω_i axis. On that axis, we have

$$n(i\omega_i) = (\varepsilon(i\omega_i))^{1/2} = \left(1 + \frac{2}{\pi} \int_0^\infty \frac{x\varepsilon_2(x)dx}{x^2}\right)^{1/2} \quad [18]$$

$n(i\omega_i)$ decreases monotonically from $n(0)$ to 1 when ω_i increases from 0 to infinity (Landau and Lifshitz, 1977). The condition $n(i\omega_i) - N_D = 0$ will be satisfied somewhere on the imaginary axis, if $n(0) > N_D$. As shown later in the experimental section, this condition is satisfied for ices at high pressures. Modifications needed to apply the KK procedure correctly will be discussed later in the text. It is useful to point out here that a

very simple way to account for the Blaschke product is to solve for the condition $n(i\mu_n) - N_D = 0$ numerically (using eqn [18]) and dielectric function from the oscillator fit (eqn [1]). Another possibility is to apply the KK procedure self-consistently, by iteratively adjusting the Blaschke root μ_n .

2.13.3.2 Electronic Excitations

2.13.3.2.1 Extended excitations

Interband transitions are electronic excitations between bands, whereas intraband transitions are those within a band. An example of the latter is the damped frequency dependence of electronic excitations associated with itinerant electrons in a metal (which by definition has a partially filled band). The collective longitudinal excitations of the conducting electrons are known as plasma oscillations. Plasma oscillations (plasmons) can be excited by inelastic scattering techniques at high pressures. Plasmons can also be excited in materials with a bandgap (i.e., dielectrics), typically at higher energies. In olivines, the bandgap varies from 7.8 eV in forsterite to 8.8 eV in fayalite (Nitsan and Shankland, 1976).

2.13.3.2.2 Excitons

Electronic excitations may occur within the bandgap due to the creation of a bound electron-hole pair, called an exciton. The pair is characterized by a binding energy E_b , which is given by $E_g - E_{ex}$, where E_{ex} is the excitation energy. In some respects, these excitations are the equivalent of localized transitions in molecular spectroscopy, but they can propagate in a crystal and are characterized by a wavevector k . Continuing with the example of olivines at zero pressure, a prominent excitonic absorption is observed near the bandgap (Nitsan and Shankland, 1976). The absorption characteristics in this region in dense ferromagnesian silicates and oxides are important for assessing the heat transfer in the Earth, which is predominantly radiative at deep mantle temperatures.

2.13.3.2.3 Crystal field transitions

The color of many minerals arises from substitution of transition metals in the crystal structure. The substitution of transition metals in olivines at zero pressure results in a strong absorption beginning 1–2 eV below the bandgap, which is ascribed to transitions between widebands and the d-levels in the system (Nitsan and Shankland, 1976). The development and application of crystal field theory for understanding behavior of open-shell systems ions, such as partially filled d-shell of transition elements, in minerals have a long history. As discussed earlier in the text, a more fundamental quantum mechanical picture shows that orbital hybridization of the central ion and its neighbors (e.g., oxygen atoms) is significant and that the orbital splitting is not a purely electrostatic effect, but has a similar dependence on interatomic distances.

2.13.3.2.4 Charge transfer

Charge transfer represents another important class of excitations in these materials. Many of these transitions in minerals occur in the ultraviolet region (Burns, 1993). Intervalence charge transfer (e.g., metal-metal charge transfer) may occur between ions of different valence states, such as Fe^{+2} – Fe^{3+} or Fe^{2+} and Ti^{4+} . These transitions often give rise to bands in the

visible spectrum that show marked shifts with pressure (Mao, 1976).

2.13.3.2.5 Excitations from defects

Many defects are also associated with electronic properties or are electronic in origin. Electron-hole centers or defects can be produced by deformation or radiation, either naturally or in the laboratory. Examples of naturally occurring systems at ambient pressure that exhibit these properties are smoky quartz and numerous colored diamonds (see Rossman, 1988). Defect luminescence has been observed to be pressure-induced, and it may be connected with emission features observed in shock-wave experiments (see Hemley et al., 1998b).

2.13.3.2.6 Electrical conductivity

Electrical conductivity is another measure of the response of the system to an applied electric field (static or frequency-dependent). Electrical conductivity may be electronic or ionic and can be intrinsic or extrinsic. If there is a gap between the valence and conduction bands, the electronic conductivity can be thermally activated at finite temperature. This can also give rise to coupled distortions of the lattice as the electrons move through it, called small polarons (see Kittel, 1996). Naturally, electrical conductivity measurements provide a means for the direct identification of the insulator-metal transitions, induced by either pressure or temperature.

In general, electrical properties are also very sensitive to minor chemical impurities and defects in a given specimen (Tyburczy and Fiesler, 1995), such as Fe content and volatile content. The conductivity can be written as a complex quantity, giving a real and an imaginary part (loss factor); this complex function is measured by impedance spectroscopy. Grain boundary conduction, for example, is observed to decrease under pressure as grain-grain contacts increase. Ionic conductivity may be especially noticeable at higher temperatures (e.g., premelting or sublattice melting). Such behavior has been proposed for silicate perovskites by analogy to other perovskites and theoretical calculations (Hemley and Cohen, 1992).

An exciting area now is understanding conductivity in correlated metals. Transition metal oxides are examples of Mott insulators (Mott, 1990), which are insulating because of local correlations not included in the conventional band picture. At high temperatures and pressures, these materials can become metallic. The computational technology has now developed to treat these materials with many-body theory, even to compute the frequency-dependent conductivity (Ohta et al., 2012). Measurements are in good agreement with experiment. Note that the conventional view of transport in wüstite, Fe_{1-x}O , was that the conductivity was caused by defects (Gartstein and Mason, 1982; Li and Jeanloz, 1990). Although this is true at ambient conditions, we now know that in the metallic state at high pressures and temperatures, the conductivity is a bulk effect and apparently little effected by defects, as can be seen from the good agreement between defect-free many-body calculations and experiments on real, defective, wüstite.

2.13.3.3 Magnetic Excitations

Magnons are excited magnetic states that can be excited in light scattering via direct magnetic dipole coupling or an indirect,

electric dipole coupling together with spin orbit interaction (Fleury and Loudon, 1968). High-pressure measurements on mineral analogs have been performed to determine the metal-anion distance dependence of the superexchange interaction J (Struzhkin et al., 1993b). This interaction parameter is a measure of the coupling of metal anions through a (normally) diamagnetic anion, such as the O between two Fe atoms. Magnon excitations may also be observed by infrared absorption.

2.13.4 Overview of Experimental Techniques

An array of ambient pressure techniques can now be used to probe electronic and magnetic excitations in minerals. Band structure can be probed by photoemission, which involves interaction of electrons with the sample. Other such spectroscopies involving electron interactions include electron energy loss and auger (Cox, 1987), each of which have been used for studying high-pressure phases quenched to ambient conditions. Here, we focus on techniques that have been applied to deep Earth materials in situ at high pressure. Pressure generation techniques will not be discussed. A review of these methods, and specifically diamond anvil cells (DACs), is given elsewhere in this treatise. It is useful to point out briefly that new techniques, such as those based on chemical vapor-deposited diamond, are helping to advance these measurements (Hemley et al., 2005; Mao et al., 2003b; Yan et al., 2002). Cubic zirconia (Xu et al., 1996), moissanite (Xu and Mao, 2000; Xu et al., 2004), and other materials can be used as high P - T anvils. Variations on a number of these techniques can also be used for in situ measurements on dynamic compression (e.g., shock-wave) experiments (Ahrens, 1987).

2.13.4.1 Optical Spectroscopies

2.13.4.1.1 Optical absorption and reflectivity

Optical spectroscopies have been one of the principal techniques used for in situ high-pressure investigations of minerals with high-pressure devices having optical access (e.g., diamond anvil cells). A number of different types of absorption spectrometer systems, including double-beam instruments, have been designed and built for high-pressure mineral studies. In optical experiments on samples in high-pressure cells using refractive optics (lenses), there is a need in general to correct for the index of refraction of the diamond because of chromatic aberrations (wavelength dependence of the focusing). This problem can also be overcome by the use of reflecting optics (e.g., mirror objectives). Versatile UV-visible-near-IR absorption and reflectivity systems using conventional continuum light sources have been designed for high-pressure applications (Hemley et al., 1998a; Syassen and Sonneschein, 1982; Figure 1). Standard continuum sources and wide variety of laser sources that span the UV-visible and much of the IR regions are now available. Examples of optical absorption measurements on $(\text{Mg,Fe})\text{SiO}_3$ perovskite are shown in Figure 2(a) and 2(b) (Goncharov et al., 2008; Keppler et al., 2008).

The most straightforward is the measurement of the real part of the dielectric function (i.e., off-resonance), corresponding to the refractive index in the visible spectrum of

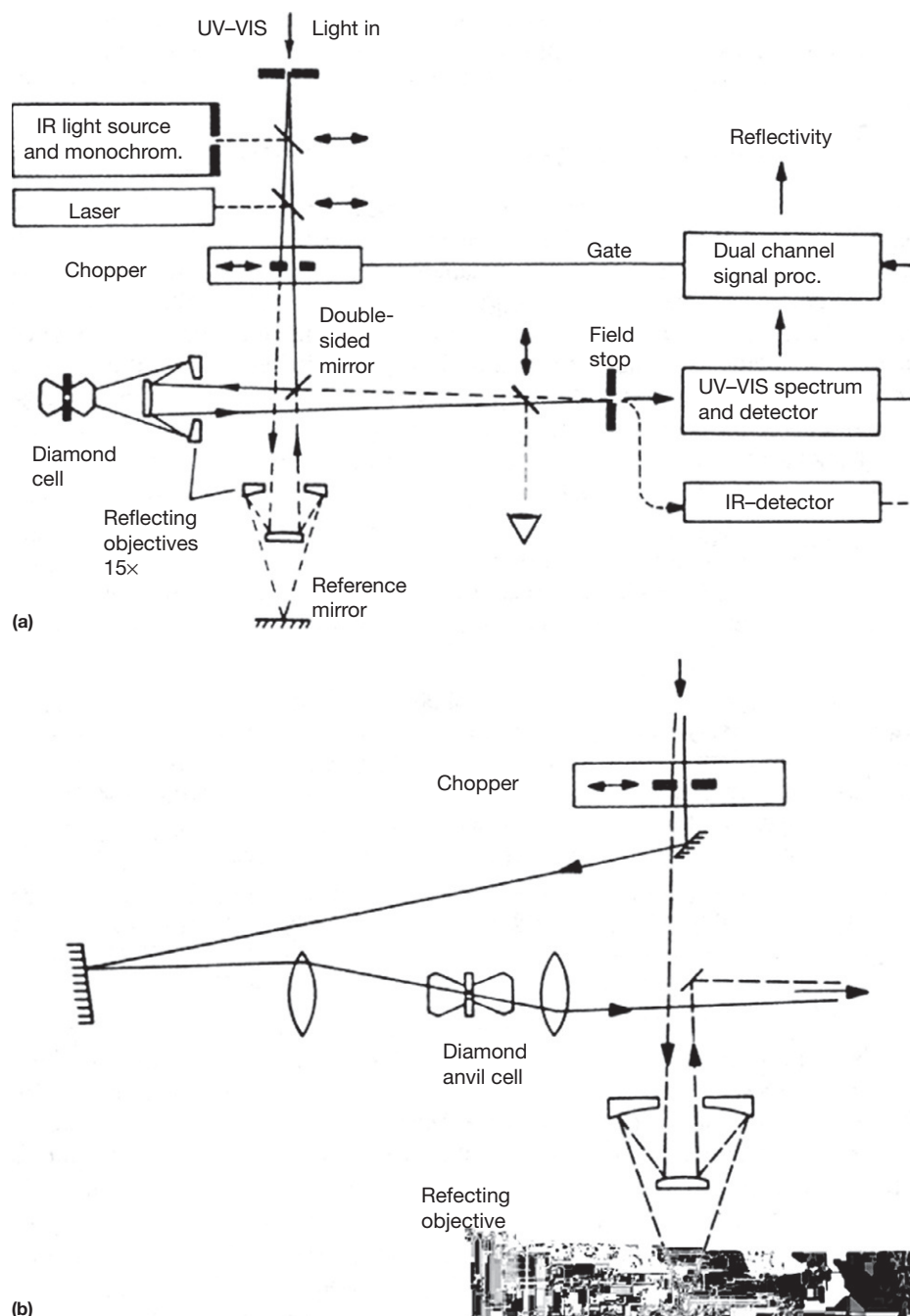


Figure 1 Example of a high-pressure UV-visible-near-IR optical setup. (a) Double-beam instrument for reflectivity measurements. Reflecting microscope optics are used to remove chromatic aberrations along with a grating spectrometer. (b) Modification of the double-beam system for absorption measurements. One of the reflecting objects is replaced by an achromatic lens. The system is capable of measurements from 0.5 to 5 eV; similar systems are in use in a number of high-pressure laboratories. Reproduced from Syassen K and Sonneschein R (1982) *Review of Scientific Instruments* 53: 644–650.

minerals that are transparent wide-bandgap insulators. Absorption (transmission) or reflectivity measurements with broadband light of thin samples of comparable thickness to the wavelength of light give rise to patterns of constructive and destructive interference in the spectrum. These fringes are straightforward to measure in a diamond anvil cell as shown in the measurements for H₂O ice (Zha et al.,

2008; **Figure 2(c)**). The spacing is determined by the refractive index and the thickness of the platelike sample; each may be determined independently if the order of the fringe is known, and this can be found in several ways. Moreover, the wavelength dependence gives the dispersion of the index, which can be related to the higher-energy electronic excitations, as described in the preceding text.

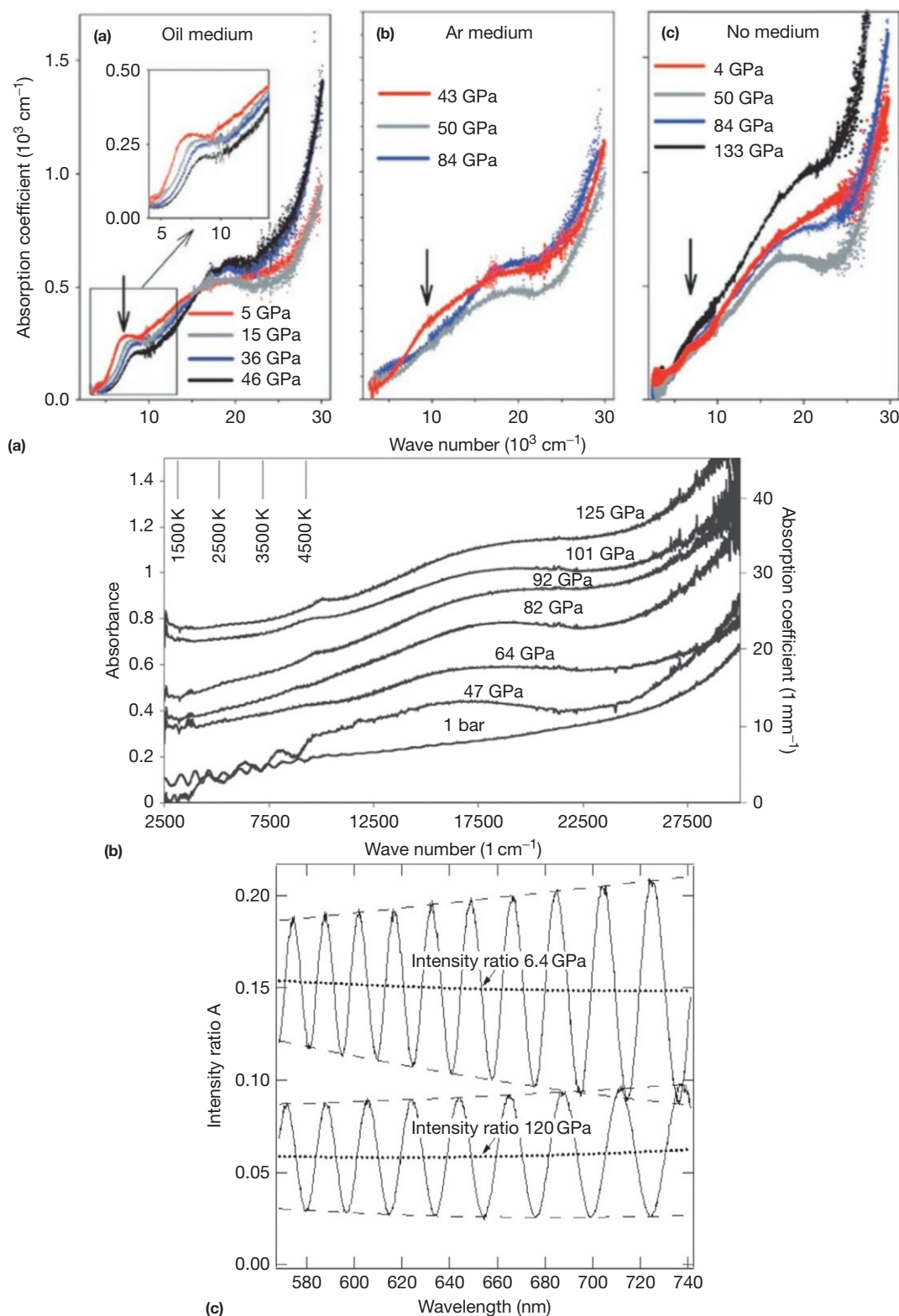


Figure 2 (a) Optical absorption spectra of silicate perovskite (10 mol% Fe) up to 133 GPa at room temperature in various pressure media. The sample thickness was measured from white-light interferometry at ambient pressure and calculated at high pressure using an isothermal equation of state. Ripples in the spectra at low pressures are interference fringes resulting from multiple reflections between the parallel polished sample surfaces. The interference patterns have been smoothed (thick solid lines) for clarity. Vertical arrows designate the Fe^{2+} crystal field transitions that are characteristic of the high-spin phase. The inset shows an enlarged view of the near-infrared spectral range. Reproduced from Goncharov AF, Haugen B, Struzhkin VV, Beck P, and Jacobsen SD (2008) *Nature* 456: 231–234. (b) Near-infrared and optical absorption spectra of silicate perovskite to 125 GPa. The 1 bar spectrum is shown as measured; the other spectra are offset vertically for clarity. Without offset, the low-frequency parts of the spectra below

Such measurements can be used to calculate effective oscillator frequencies that describe the behavior of the dielectric function as a function of pressure and temperature. For example, examples include H_2O and H_2 at megabar pressures (Hemley et al., 1991; Loubeyre et al., 2002; Zha et al., 2008). The results for H_2 are broadly compatible with direct observation of optical absorption of H_2 at pressures of >250 GPa (Loubeyre et al., 2002; Mao and Hemley, 1989, 1994). MgO and diamond both show a decrease in refractive index with pressure. From this, we infer that the bandgap of MgO increases with pressure, in agreement with theory (Mehl et al., 1988). A similar behavior is observed for hydrostatically compressed diamond (Eremets et al., 1992; Surh et al., 1992). In contrast, the bandgaps of many other materials decrease under pressure (Hemley and Mao, 1997). Also, both theory and experiment indicate that the diamond index can increase with nonhydrostatic stress. Brillouin scattering provides independent measurements of the refractive index; results for MgO are in good agreement with the interference fringe measurements (Zha et al., 1997).

2.13.4.1.2 Luminescence

High-pressure luminescence measurements give in principle the same information as does absorption and reflectivity. Luminescence includes fluorescence and phosphorescence, which correspond to shorter- and longer-lived excited states (generally defined as in the less than and greater than a nanosecond, respectively). The transitions are typically governed by dipole selection rules. For the case of atomic-like transitions, such as localized excitations of ions in crystal fields, this can be understood in terms of the Laporte selection rules (i.e., $\Delta l = \pm 1$, where l is the angular momentum quantum number). An early and particularly important application in mineralogy is the use of this technique in constraining the proportion of Fe^{2+} and Fe^{3+} in various sites in silicates from d-orbital excitations (Rossman, 1988). Charge transfer applications are described earlier in the text. Other applications include excitations near and across bandgaps and excitations associated with defects.

Luminescence measurements are of obvious importance in the calibration of pressure. This includes excitation of Cr^{3+} in ruby by UV-visible lasers (e.g., He-Cd, Ar^+ ion, and doubled Nd-YAG) and measurement of the calibrated shift of the R_1 line in luminescence, currently calibrated to 180 GPa (Bell et al., 1986; Mao et al., 1978, 1986). The recent use of tunable lasers (e.g., titanium-sapphire) and pulsed excitation techniques has allowed the extension of the measurements of ruby luminescence to above 250 GPa (Goncharov et al., 1998). Other luminescent materials, such as Sm-doped yttrium aluminum garnet, have been calibrated for this pressure range (Liu and Vohra, 1996) and for high temperatures at lower

pressures (Hess and Schiferl, 1992). Other applications include the study of vibronic spectra, which are combined (coupled) electronic and vibrational excitations. Measurements at high pressure reveal the pressure dependence of both the electronic and vibrational levels in the system, which can be used to determine acoustic velocities (given the assumptions about the dispersion of the modes and correct assignment of typically complex spectra; e.g., Zhang and Chopelas, 1994). There has been continued work on pressure calibration with optical spectroscopic methods (Goncharov et al., 2005b).

2.13.4.1.3 Infrared spectroscopy

Infrared spectroscopy is an extension of optical spectroscopy that typically involves different techniques (e.g., Fourier transform spectroscopy). In addition, the use of synchrotron radiation for infrared spectroscopy has been shown to be particularly useful for small samples such as those in high-pressure cells (Figure 3(a)). The technique can be used to study electronic and magnetic excitations, insulator-metal transitions, crystal field and charge transfer transitions, and, for metals, interband and intraband transitions (Hemley et al., 1998a). Optical studies under pressure, especially reflectivity and absorbance, provide unique information important for understanding fundamental changes in the electronic structure of these systems close to the insulator-metal transition because of the broad spectral range that extends to long wavelengths (low wave numbers). It can also provide unique information on magnetic excitations (Struzhkin et al., 2000). This study showed how the pressure dependence of the IR and Raman modes can be used to distinguish between magnon and electronic excitations. In addition, infrared vibrational spectral profiles contain information on the electronic properties, that is, through the KK transformation. An example of reflection spectra and the transformed data is shown in Figure 3(b) and 3(c).

2.13.4.1.4 Raman scattering

Although most commonly used to study vibrational dynamics, laser light-scattering spectroscopies can also be used to investigate high-pressure electronic and magnetic properties (Figure 4). Raman and Brillouin spectroscopies are inelastic light-scattering techniques that measure transitions to an excited state from the ground state (Stokes scattering) and to the ground state from a thermally excited state (anti-Stokes scattering). Low-frequency crystal field excitations of the appropriate symmetry can be probed, and the pressure dependence of such transitions has been studied in a few cases (Goncharov et al., 1994). The conduction electrons in metals can also be probed by Raman scattering, which in general gives rise to weaker broader features in the light-scattering spectrum. High-pressure studies are complicated by the need of

7500 cm^{-1} would nearly coincide. Sample thickness at ambient pressure is $30\text{ }\mu\text{m}$. The absorption coefficients are based on the decadic logarithm and normalized to this sample thickness. Because of the compression of the sample, the absorption coefficients increase by about 9% relative to these values at 125 GPa. To obtain absorption coefficients based on the natural logarithm (i.e., eqn [2]), the scale needs to be multiplied with $\ln 10 = 2.30$. The position of the maxima of thermal blackbody radiation at different temperatures is also shown for reference. The slight oscillations at low frequency in some spectra are artifacts (interference fringes). The small peak seen in some spectra close to $10\,000\text{ cm}^{-1}$ is probably not real; it is likely related to the change in detector close to this frequency. Reproduced from Keppler H, Dubrovinsky LS, Narygina O, and Kantor I (2008). (c) Pressure dependence of the reflectivity of H_2O ice relative to diamond. *Science* 322: 1529–1532; and from Zha CS, Hemley RJ, Gramsch SA, Mao HK, and Bassett WA (2008) *Journal of Chemical Physics* 126: 07450.

discriminating the spurious background contaminations from the true electronic contribution. Superconductivity in metals gives rise to structure in the electronic Raman spectrum, such as gap-like features at low frequency (Zhou et al., 1996).

Such studies include magnetic transitions in AFM materials such as transition metal oxides predicted to undergo high-pressure insulator-metal transitions. These materials have magnetic anomalies that may be difficult to study directly at

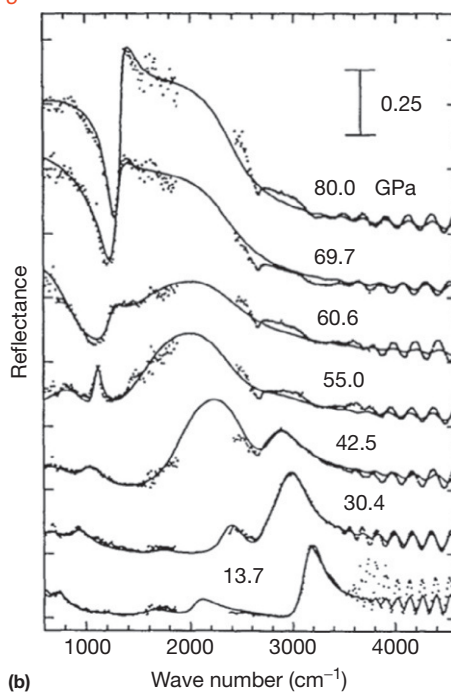
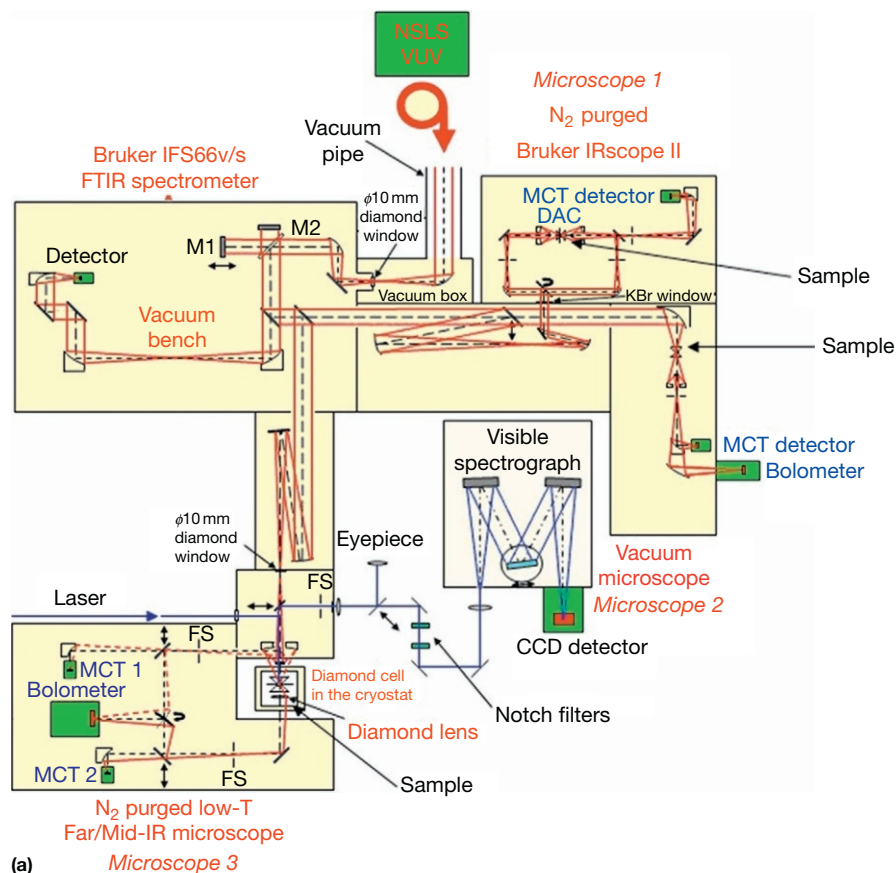


Figure 3 (continued)

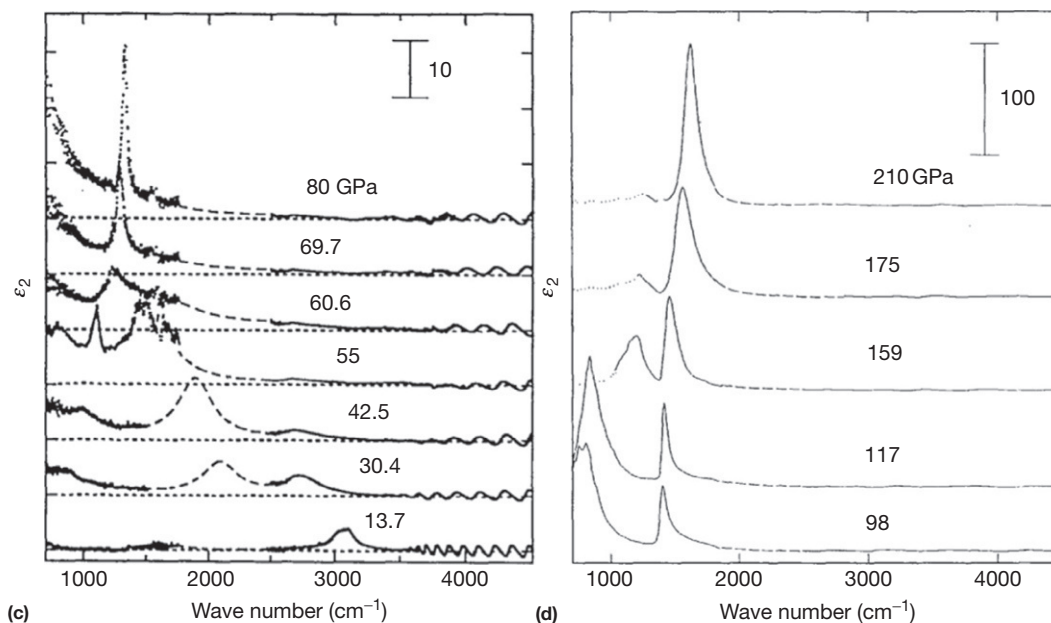


Figure 3 (a) Schematic of the high-pressure synchrotron infrared spectroscopy facility at the National Synchrotron Light Source (Beamline U2A). Three different microscopes are optically interfaced with the spectrometers. The sample is located within the high-pressure cell designated by diamond anvil cell or DAC. (b) Representative reflectivity spectra: points, experimental data; lines, oscillator model. Spectra are shifted with 0.25 unit increments in the vertical direction. There are no data in the range of the strong diamond absorption (1800–2400 cm⁻¹). Spurious oscillations at high frequencies originate from the Fabry–Pérot interference between the diamond anvil cells. The spectral region around 2600 cm⁻¹ is complicated by the absorption of diamonds. Peculiarities in the spectra are due to incomplete cancellations of sharp features in reference and sample spectra. Reproduced from Goncharov AF, Struzhkin VV, Somayazulu M, Hemley RJ, and Mao HK (1996) *Science* 273: 218–220. (c) Imaginary part of the dielectric constant ϵ_2 of H₂O obtained from a Kramers–Kronig (KK) analysis of reflectivity spectra: points, KK transformation of experimental data; dashed lines, oscillator fit. The curves are offset in the vertical direction for clarity. Reproduced from Goncharov AF, Struzhkin VV, Somayazulu M, Hemley RJ, and Mao HK (1996) *Science* 273: 218–220. (d) ϵ_2 spectra of the H₂O (295 K) showing the positive pressure shift of the stretching mode to ν_s 210 GPa. Reproduced from Goncharov AF, Struzhkin VV, Somayazulu M, Hemley RJ, and Mao HK (1996) *Science* 273: 218–220.

high pressure, but these anomalies may be associated with pronounced changes in magnetic light-scattering spectra. These excitations have a strong temperature dependence because of the large temperature dependence of magnetic ordering (Struzhkin et al., 1993a). A large number of excitations are observed, including several very strong bands, all of which can be described by the appropriate Hamiltonian. Measurements of the two-magnon excitations in Fe₂O₃ and NiO by high-pressure Raman scattering constrain the magnetic properties of these materials at high density (Massey et al., 1990a,b). The pressure dependence of higher-order effects such as the coupling of the phonons with electron spin-pair excitations and the electronic structure of the material can also be probed (Massey et al., 1992). Although the higher-temperature behavior of such materials is of direct concern for the deep Earth (i.e., along the geotherm), detailed characterization of the low-temperature ground state is essential for understanding higher-temperature properties. The extremely low background signal in light-scattering experiments using ultrapure synthetic single-crystal diamond anvil cells (Goncharov et al., 1998) is enabling the extension of these light-scattering studies of electronic and magnetic excitations to a wider class of materials, including opaque minerals and metals. This is illustrated by high-pressure measurements on oxide superconductors, which can be considered analogs of

dense oxide perovskite and perovskite-like planetary materials (Cuk et al., 2008; Figure 5).

2.13.4.1.5 Brillouin and Rayleigh scattering

In principle, other optical light-scattering techniques can be used to investigate electronic and magnetic phenomena at high pressure. Brillouin scattering involves the measurement of acoustic phonons; in metals, the measurements correspond to surface modes or plasmons. Brillouin scattering can also be used to determine the pressure dependence of the refractive index (dielectric function), usually in transparent materials. Rayleigh scattering is a quasi-elastic scattering spectroscopy; it has been used less in high-pressure studies of materials because of the difficulty of obtaining accurate measurements due to typically strong background scattering near the excitation wavelength (laser line) by the anvils in the high-pressure cell.

2.13.4.1.6 Nonlinear optical methods

One of the limitations of conventional one-photon absorption, reflectivity, and luminescence measurements is the fact that the absorption threshold of the anvils of the high-pressure cell precludes measurements on samples at higher energies (e.g., in the ultraviolet range), as mentioned in the preceding text. Nonlinear optical techniques can be used to access this region, however. For example, one can perform three-photon

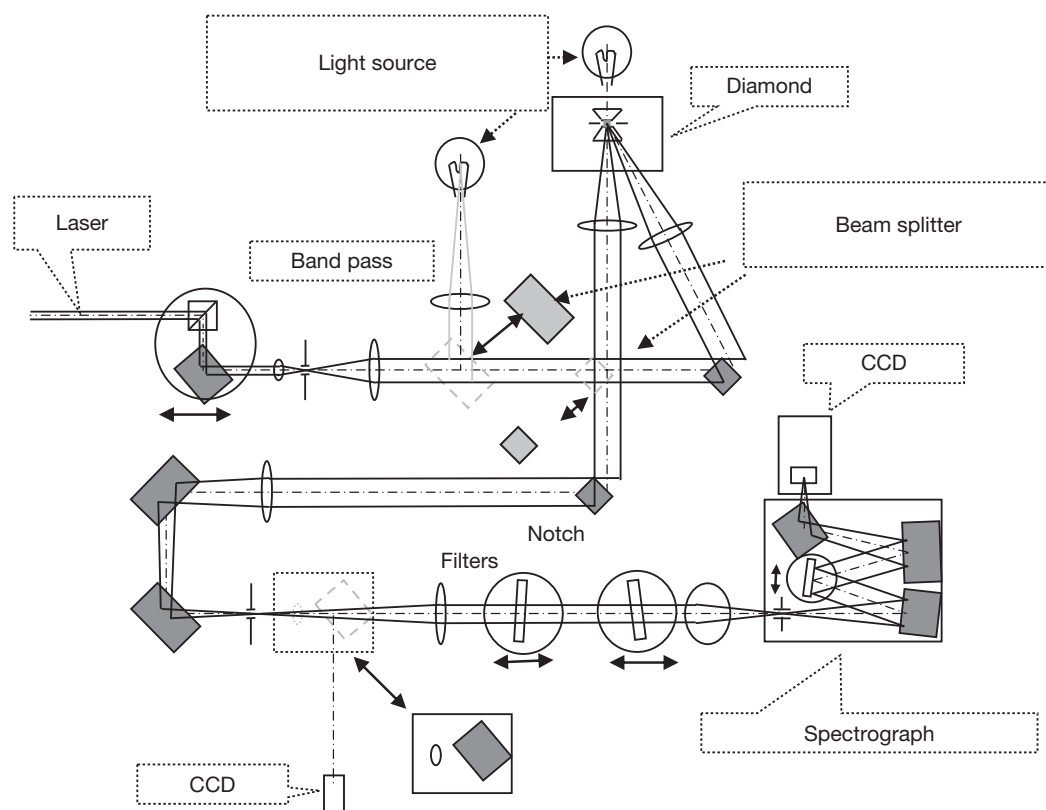


Figure 4 Schematic of a high-pressure Raman scattering system. The excitation wavelength can be easily tuned without changing the holographic optics and consequent realignment of the whole system; use of holographic transmission gratings (notch filters and band-pass filters) at wavelengths other than nominal does not typically result in a deterioration of the system's performance. Rapid changes in both the excitation wavelength and the spectral range are essential for high-pressure spectroscopy. The second important distinction of the system is that it allows rapid modifications of the scattering geometry to be made. In the case of a transparent sample or if the sample is heterogeneous or very small (e.g., at multimegabar pressures), the backscattering geometry in combination with a confocal spatial filter is probably the best choice. For nontransparent and highly reflective samples, a quasi-backscattering (or angular) geometry may be employed. This arrangement has the advantage that the specular reflection (or direct laser beam in the case of forward scattering) is directed away from the spectrometer. Compared with the backscattering geometry, this expedient reduces the overall background and allows the observation of lower-frequency excitations. In the case of metals, use of the angular excitation geometry can be crucial. To be compatible with this geometry, it was necessary to modify the DAC to allow off-axis entry of the incident light. Specially designed tungsten carbide seats having angular conical holes have been used for this purpose. Use of double-spatial filtering (one for the laser and one for the signal) effectively suppresses laser plasma lines and unwanted Raman/fluorescence signals. In this configuration, the laser spot can be made very small (e.g., 2 μm), and the depth of focus substantially reduced. Thus, the Raman signal from the diamond anvil cell is suppressed. Also, the effects of pressure inhomogeneity can also be substantially obviated. Use of synthetic ultrapure anvils can further reduce diamond fluorescence. This is crucial for studies of very weak scatters and/or materials at very high pressures (above 200 GPa), where strong stress-induced fluorescence of the diamond anvil cells can be a major obstacle to the acquisition of Raman or fluorescence spectra.

excitation of valence electrons to the conduction band or excitonic states in the vicinity of the conduction band, which is above the one-photon threshold of the anvil; this has been achieved in compressed salts in sapphire anvil cells (Lipp and Daniels, 1991). It is now possible to apply and extend these techniques to study to high-pressure minerals. Another category of techniques in this class is four-wave mixing experiments, such as coherent anti-Stokes Raman scattering (CARS). These rely on the third-order susceptibility and are enhanced when there are two-photon electronic resonances.

CARS is a nonlinear optical technique whereby a pump beam ω_p and a Stokes beam ω_s are mixed via third-order susceptibility to generate enhanced anti-Stokes emission. Enhanced anti-Stokes emission is observed when the narrow-band pump and Stokes beams are detuned such that their

difference frequency ($\omega_v = \omega_p - \omega_s$) corresponds to vibrational sideband. A resonantly enhanced signal is emitted in the presence of the second pump photon at the frequency $\omega_{\text{CARS}} = 2\omega_p - \omega_s$, subject to momentum conservation (phase matching) of the four-wave mixing process. Signal generation in CARS is coherent, with an intensity that grows quadratically with interaction length, unlike incoherent spontaneous Raman, where intensity grows linearly with interaction length. In order to achieve this enhancement, the pump and Stokes pulses must spatially and temporally overlap at the sample. Moreover, anti-Stokes emission is directional due to phase matching. The Stokes beam may be narrowband, which gives an anti-Stokes response at the difference between the pump and Stokes beams (which may be scanned), or broadband, where a broadband anti-Stokes spectrum may be detected in

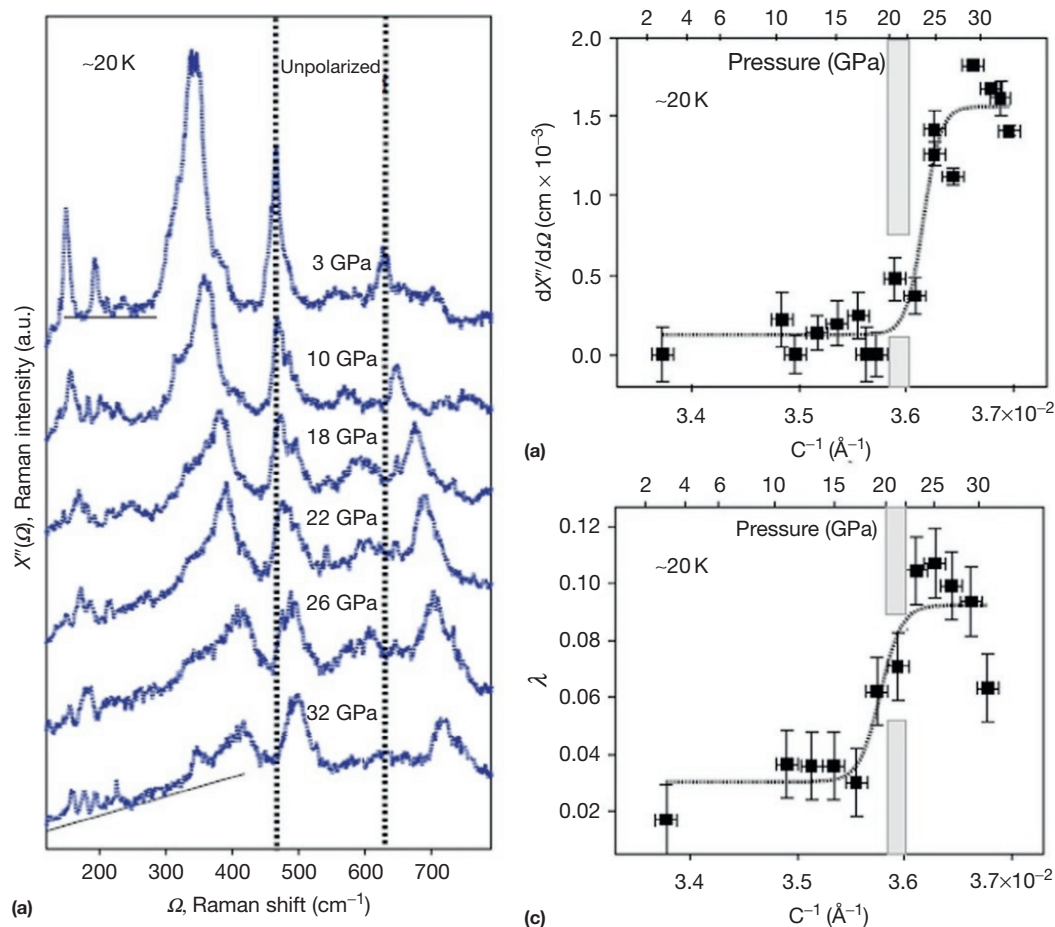


Figure 5 (a) Raman spectra of the B_{1g} phonon, O–Bi phonon in the Bi–O block layer, and the apical oxygen phonon at ~ 20 K with pressure. (b) Slope of the linear electronic background from 200 to 300 cm^{-1} at ~ 20 K. Spectra at each pressure were normalized to the intensity at 850 cm^{-1} . (c) The full Raman vertex, using a normal-state electronic background, was fit to 20 K data to derive the electron–phonon coupling parameter λ . Reproduced from Cuk T, Struzhkin VV, Devereaux TF, et al. (2008) *Physical Review Letters* 100: 217003.

a spectrometer. The previously mentioned considerations are important for choosing a correct experimental strategy in the case of the DAC. CARS spectroscopy has been used to study molecular materials under extreme conditions generated by shock waves. High-quality spectra have been obtained using a single (combined) laser pulse of several nanosecond duration. As described earlier in the text, in this experiment, the entire CARS spectrum is measured simultaneously using a broadband Stokes pulse. Similar techniques have been used in DAC studies. The overall CARS cross section is determined by the $\chi^{(3)}$ susceptibility, a nonlinear electronic property.

2.13.4.2 Mössbauer Spectroscopy

Mössbauer spectroscopy probes the recoilless emission and resonant absorption of γ -rays by nuclei (Mössbauer, 1958). The energy levels of the nuclei are sensitive to the electrostatic and magnetic fields present at the nuclei and thus to changes in chemical bonding, valence (i.e., the oxidation state of an atom, ferrous versus ferric), and magnetic ordering. Mössbauer spectroscopy reveals information on the hyperfine interactions and the local electronic and magnetic fields at a nucleus. Only a few nuclei exhibit the Mössbauer effect (e.g., ^{57}Fe , ^{119}Sn , ^{121}Sb , ^{153}Eu , and ^{197}Au), and the great majority of applications

in Earth science (and in general) are with ^{57}Fe . The natural abundance of ^{57}Fe is 2.1%, so some studies require enrichment of ^{57}Fe to obtain a stronger signal. The technique has been used extensively in the mineralogy of deep Earth materials, including in situ high-pressure measurements. A typical probe for mineral systems is based on the reaction $^{57}\text{Co} + {}^0\beta^{57} \rightarrow \text{Fe} + \gamma$. In a conventional Mössbauer experiment, one modulates the energy of the γ -rays by continuously vibrating the parent source to introduce a Doppler shift of the radiation (see Dickson and Berry (1986) for an introduction to Mössbauer spectroscopy and McCammon (1995) for a review of applications to minerals).

The isomer shift is the shift in the nuclear energy level and corresponds to the source velocity at which maximum absorption appears. The electric quadrupole splitting arises from the interaction between the nuclear moment and quadrupole splitting and the local electric field gradient at the nucleus. This occurs for nuclei with spin quantum number $I > 1$ (i.e., for ^{57}Fe , $I = 3/2$). The hyperfine field is due primarily to the contact interaction between electrons at the nucleus and the nucleus, rather than to the macroscopic magnetic field in a material. A hyperfine field arises from different densities of spin up and down electrons at the nucleus.

Applications include determination of Curie and Néel transition temperatures, valence state, site occupancy, and local

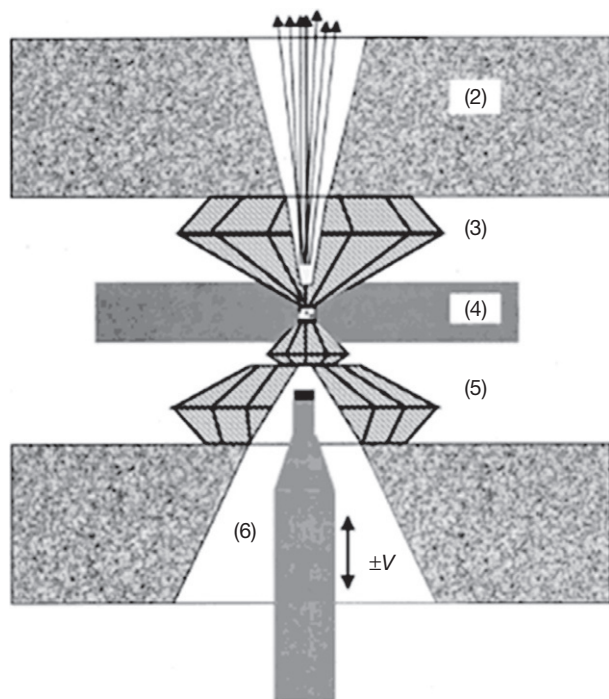


Figure 6 A sketch depicting the setup for high-pressure Mössbauer studies using perforated diamond anvil cells (see Dadashev et al. (2001) for details).

order. In studies of deep Earth materials at high pressure, each of these can be probed as a function of pressure (and temperature), including the measurement of changes across various transformations (crystallographic, electronic, and magnetic). Instrumentation consists of a radioactive source, vibrating drive, and detector (scintillator or proportional counter). Recent examples of high-pressure studies include measurements on a series of pyroxenes to 10 GPa (Zhang and Hafner, 1992) and measurements on $\text{CaFeSi}_2\text{O}_6$ to 68 GPa, which revealed evidence for a phase transition associated with a change in spin state. The Mössbauer technique has been extended into the megabar pressure range as discussed later in the text for FeO (Pasternak et al., 1997b; Figure 6). The Mössbauer studies on FeO along with acoustic sound velocity measurements show fascinating interplay between magnetic ordering and elasticity (Kantor et al., 2004b).

2.13.4.3 x-Ray and Neutron Diffraction

2.13.4.3.1 x-Ray diffraction

Crystal structures are determined by the system optimizing the interactions of electrons and nuclei and thus by details of bonding interactions between atoms; thus, crystallography is an essential mean for studying bonding and evolution of atomic interactions with pressure (Wyckoff, 1923). x-Ray diffraction relies on the interaction between x-rays and electron distributions in materials, so in principle, it can give the real-space charge density, but this requires high-quality crystals, corrections for absorption, and measurements to high q . The charge density includes smearing from atomic motions, which must be modeled and subtracted to obtain useful information. Few experimental charge densities have thus been obtained;

one successful study was on stishovite (Spackman et al., 1987). Changes in electron density associated with crossing insulator–semiconductor–metal transitions can be identified (Fujii, 1996; Shen et al., 2012). Recently, a new method, the maximum entropy method (MEM), has been developed as a practical technique for solving crystal structures. Based on information theory and using Bayesian statistics, it builds electron density through constrained entropy maximization. The MEM statistically estimates the most reliable electron density distribution from the finite observed structure factors, removing the problem caused by the termination effect in the difference Fourier synthesis. Recent work has included studies of oxides by Yamanaka (2007) and changes in electron density across spin transition of Fe^{2+} in ferropentacite (Ikuta et al., to be published). The advent of third-generation synchrotron radiation sources and modern area detectors is potentially important for extending these measurements to deep Earth materials at very high pressures. As discussed in the preceding text, pressure can induce complex crystal structures in simple elements, in principle yielding detailed information about atomic interactions. Because this structural complexity is driven in part by bonding and electronic structure, detailed understanding of this real-space atomic structure of these phases provides insight into the electronic structure. The latest developments in single-crystal x-ray diffraction at high pressure and high temperature have benefited greatly from advances in large opening designs of DAC (Boehler et al., 2013) and high-energy x-ray sources, which allows collecting single-crystal diffraction data at pressures above 100 GPa and at temperatures above 1000 °C (Boffa Ballaran et al., 2013; Dera et al., 2013). In addition to the single-crystal diffraction, intensity information in powder diffraction is now widely used for structure refinement via the Rietveld (1966) method. It must be noted that the Rietveld method does not provide the initial model to be refined. Traditional methods of structure analysis, such as Patterson synthesis or direct methods, are often used to establish the basic features of the structure, after which the Rietveld refinement can be carried out. Recently, many successful structure predictions have been made by the first principles (e.g., Oganov, 2010; Wang and Ma, 2014). These theoretical predictions provide important basic models in further structure refinement with experimental data. With the developments in microbeam technology in synchrotron radiation, the minimal size needed for single-crystal diffraction has been reduced to around 1 μm . Traditional powder sample may be treated as multiple grains. A new tool of ‘multigrain crystallography’ has been recently developed with the quality of the resulting refinements comparable with single-crystal work (Sørensen et al., 2012). The multigrain approach holds great potentials for crystallographic studies of deep Earth materials, as demonstrated recently by a study of single-crystal structural determination of $(\text{Mg,Fe})\text{SiO}_3$ postperovskite (Zhang et al., 2013).

2.13.4.3.2 Neutron diffraction

Neutron scattering is complementary to x-ray scattering, and it has the advantages relative to x-ray scattering by virtue of its sensitivity to low- Z elements, angle-independent form factor, high penetrating power, and sensitivity to magnetic order. Because the scattering amplitude of neutrons by an atom depends on the direction of its magnetic moment, neutron diffraction can be used to map out the orientation of the

magnetic moments in the unit cell of a crystal. There have been a growing number of in situ high-pressure measurements on minerals (Parise, 2006). Advances have been made possible by the development of new classes of high-pressure devices, notably the Paris–Edinburgh cell and various types of gem anvil

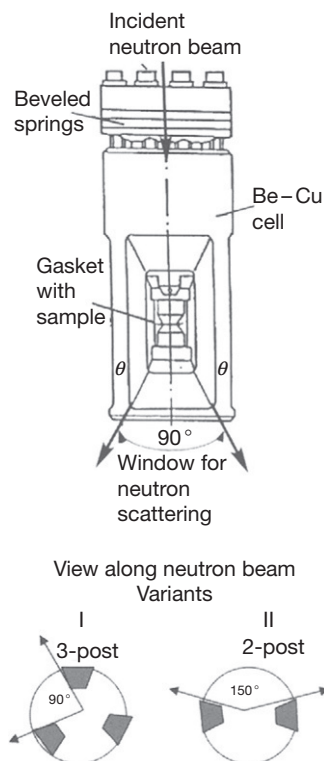


Figure 7 A variation of the 'gem cell.' Reproduced from Ivanov AS, Goncharenko IN, Somenkov VA, and Braden M (1995) *Physica B* 213: 1031–1033.

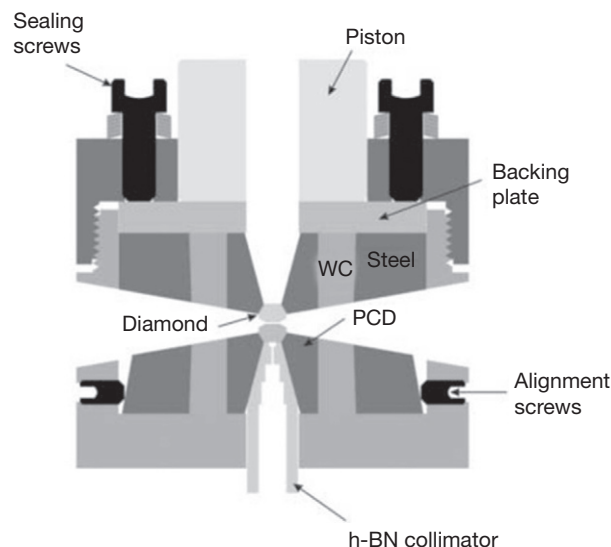


Figure 8 Schematic of a new diamond anvil cell accommodating binding ring supports for conical anvils for high-pressure neutron scattering. Reproduced from Boehler R, Guthrie M, Molaison JJ, et al. (2013) *High Pressure Research* 33: 546–554.

cells (Figures 7 and 8). An example is the high-pressure polymorphism of FeS in which the transformation to FeS II at 3.4 GPa was found to be associated with a spin-reorientation transition (Marshall et al., 2000). A second example is Fe_2O_3 , for which the AFM ordering can be tuned by pressure (Goncharenko et al., 1995; Parise, 2006). High-pressure neutron scattering of FeO carried out with gem anvil cells revealed a surprising absence of long-range magnetic order to 20 GPa (Ding et al., 2005).

The coupling of phonons with the high-spin/low-spin transitions can be observed by x-ray techniques (Schwoerer-Bohning et al., 1996). Inelastic neutron scattering can also be used to excite magnetic transitions; it requires high energies and the measurement of low-momentum transfer. Measurements of crystal field transitions at zero pressure have been reported (Winkler et al., 1997). Given the intensity of current neutron sources, large samples are required.

2.13.4.4 Inelastic x-Ray Scattering and Spectroscopy

Advances in synchrotron radiation techniques have resulted in significant developments in x-ray spectroscopy, as well as diffraction, of minerals and related materials under pressure. x-Ray spectroscopies can be used as a probe of electronic structure; these techniques thus constitute an alternative to methods requiring the use or measurement of charged particles interacting with a sample (e.g., electrons in photoemission). As such, x-ray spectroscopies can be used for in situ study of properties such as band structures and local electronic structure.

Applications to mineralogy and geochemistry of Earth materials in the near-surface environment have been described previously (Brown et al., 1988). The applications at high pressure were reviewed since 1998 (Hemley et al., 1998b). Prior to this, very little x-ray spectroscopy had been conducted under pressure, and most of it has been limited to x-ray absorption spectroscopy (XAS). With new developments, the following methods are being used and/or developed for high-pressure studies of geophysically important materials: x-ray emission spectroscopy (XES), XAS, x-ray magnetic circular dichroism (XMCD), x-ray inelastic near-edge spectroscopy (XINES), electronic inelastic x-ray scattering (EIXS), resonant inelastic x-ray scattering (RIXS), Compton scattering (CS), nuclear resonant forward scattering (NRFS), nuclear resonant inelastic x-ray scattering (NRIXS), and phonon inelastic x-ray scattering (PIXS).

These x-ray intensity-limited techniques have become practical with the arrival of the third-generation high-energy synchrotron sources. Since higher pressures are reached at the expense of diminishing sample volume, the pressure limit of these experiments depends upon the ability of passing the maximum number of photons into a microscopic sample volume. The development of high-pressure x-ray spectroscopy has also been hindered by the opaqueness of high-pressure vessels. Recently, third-generation sources have greatly boosted the intensities, and new high-pressure techniques such as the development of high-strength but x-ray transparent Be gaskets have extended the window for measurements from 12 keV down to 4 keV. This extended x-ray energy range allows the study of pressure-induced effects on atomic coordination,

crystal structures, and electronic properties of a wider class of minerals using a variety of x-ray spectroscopies. The region below 4 keV (e.g., soft x-ray and vacuum ultraviolet) is still opaque in all kinds of high-pressure devices; however, inelastic scattering techniques provide a means to access states that cannot be probed by direct (one-photon) processes due to the opaqueness of the anvil and gasket (e.g., in the soft x-ray region).

2.13.4.4.1 x-Ray absorption spectroscopy

In XAS, incident x-ray is absorbed when its energy exceeds the excitation energy of deep-core electrons of a specific element in the sample, causing an atomic edge-like absorption spectrum. Near-edge x-ray absorption fine structure (XANES) (Ablett et al., 2003) provides information on symmetry-projected conduction band density of states (DOS), while the extended x-ray absorption fine structure (EXAFS) (Buontempo et al., 1998; Pascarelli et al., 2002) provides local structure information. XAS is typically monitored by broadband fluorescence. Different spectral regions in the vicinity of a core-level absorption edge are typically defined on the basis of the different information they contain. EXAFS arises from multiple scattering of electrons in the environment of an atom, from which local structural information (interatomic distances and coordination) is obtained. Spin-dependent XAS can reveal magnetic properties even in the absence of long-range magnetic order (Hämäläinen et al., 1992).

These element-specific probes reveal electronic and structural changes at high pressure (Itie et al., 1992). XAS was one of the first x-ray spectroscopy techniques applied at high pressure (Ingalls et al., 1978), but was previously limited to higher energies due to the absorption of diamond anvil cells. Both techniques extend XAS down to 4 keV that covers K-edges of first-row transition elements and L-edges of rare earth elements. XAS instrumentation is among the simplest in high-pressure x-ray experiments. Only the monochromator needs to be scanned across the specific energy edge of the element of interest. The monochromatic x-rays are focused by mirrors (e.g., meter-long K-B type) upon the sample in the cell. The absorption is measured by monitoring the intensity change of either the transmission or the fluorescence signals due to the absorption/reemission process and is normalized relative to a reference intensity measured before the sample. The large, high-demagnification, K-B mirrors provide sufficient intensity, with the beam diameter matching the small sample size at ultrahigh pressure.

High-pressure XAS has been used successfully for transition elements at moderate pressures with boron carbide anvils (Wang et al., 1998) and for higher-Z materials (Itie et al., 1992; Pasternak et al., 1997a; Zeng et al., 2010). EXAFS is now well developed for high-pressure studies (Hong et al., 2009; Ishimatsu et al., 2012; Itie et al., 1997) and can be measured by absorption or fluorescence. In addition, the Laue diffraction of single-crystal diamonds causes sharp absorption peaks that are detrimental to the EXAFS spectroscopy. To greatly reduce the diamond in the beam path, holes can be drilled in diamond anvil cells, as used in the Bassett-type hydrothermal diamond anvil cell for studying ions in aqueous solutions at moderate P - T conditions (Anderson et al., 2002; Bassett et al., 2000), and alternative beam path through high-strength beryllium and boron gaskets is used in

megabar panoramic diamond anvil cells (Mao et al., 2003a). Early high-pressure work with diamond anvil cells was limited by the Bragg diffraction from the diamond and by the absorption edge of the diamond and the gasket. Because of the low energy of the Si edge, high-pressure studies of germanate analogs have been carried out (Itie et al., 1989). The development of more transparent gaskets has helped to overcome these problems. High-quality XANES (Zeng et al., 2010) and EXAFS (Mayanovic et al., 2007) data have been collected for transition metals in DAC experiments with energies between 5 and 15 keV. In studying absorption edges over 30 keV, XAS data from a DAC are contaminated by diffraction from single-crystal diamond anvil cells. Using nanodiamond as anvil material, the contamination from single-crystal diffraction can be avoided (Ishimatsu et al., 2012). EXAFS is particularly useful for studying the pressure effects on the structures of liquids (Katayama et al., 1998; Ohtaka et al., 2004) and amorphous solids (Baldini et al., 2010; Mobilio and Meneghini, 1998). A notable example is the observation of the coordination change in crystalline and amorphous GeO_2 (Baldini et al., 2010; Itie et al., 1989). Mobilio and Meneghini (1998) provided a review of the variety of synchrotron-based x-ray techniques for studying amorphous materials, including techniques such as anomalous scattering that can be used in conjunction with EXAFS.

An energy-dispersive XAS technique has been developed (Pascarelli and Mathon, 2010), in which a focused polychromatic beam ($\sim 5 \mu\text{m}$) of extremely high flux passes a sample and is collected by an energy-dispersive detector capable of fast capturing the XAS signals at microsecond level (Andrault et al., 2010; Boehler et al., 2009). The fast measurement and small beam size in this technique allow for mapping XAS images by scanning the sample position (Aquilanti et al., 2009).

2.13.4.4.2 x-Ray emission spectroscopy

In this technique, deep-core electrons in the sample are excited by x-rays. The core holes then decay through either radiative or nonradiative processes. For deep-core holes, the dominant decay channels are radiative processes, producing fluorescence, which is analyzed to provide information on the filled electronic states of the sample. The information provided by XES is complementary to that provided by XAS on valence electrons and unoccupied states. Moreover, the final state of the fluorescent process is a one-hole state, similar to the final state of a photoemission process. Thus, the most important information provided by photoelectron spectroscopy, that is, large chemical shifts in the core-level binding energies and the valence band DOS, is also available in XES.

The energies of the fluorescent photons are analyzed with subelectronvolt energy resolution of the emission spectral line shape to provide information on the filled electronic states of the sample. As for XAS, the development of panoramic diamond anvil cells has extended the low end of the high-pressure energy window down to 4 keV (Lin et al., 2003a; Mao et al., 1998). Deep-core electrons of all elements above Ca can now be studied at high pressure by a suitable choice of analyzer crystals. For instance, transition-element ions, with their variable valence and magnetic states, control major geochemical processes and geophysical behaviors, such as oxidation,

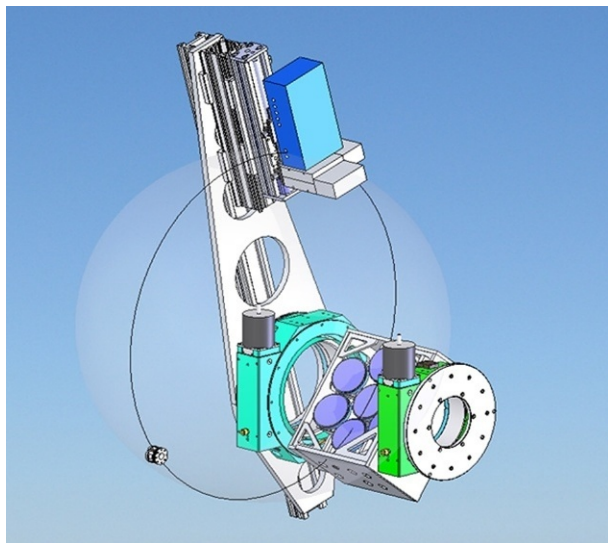


Figure 9 A 1 m Rowland circle spectrometer equipped with the 7-element analyzer system at High Pressure Collaborative Access Team (HPCAT) sector at the Advanced Photon Source. DAC, detector, and analyzers are along the circle, with precise controls of θ and 2θ for synchronized scans.

reduction, chemical differentiation, elasticity, geomagnetism, conductivity, and radiation heat transfer.

In XES experiments, the incident beam impinges on the sample, the emission x-radiation can be collected at any direction, and high-resolution emission spectra are obtained by a synchronized θ – 2θ scan of the analyzer and the detector. A high-resolution Rowland circle spectrometer is often used. Because emission signals can be collected at any direction, multiple analyzers may be used to increase solid angle coverage in data collection and thus the signal level (Figure 9). Recently, a short-distance spectrometer of large solid angle coverage has been developed, with which data collection time in XES is reduced from hours to only several minutes (Pacold et al., 2012). The excitation x-ray source only needs to have a higher energy than that of the fluorescent photons; the energy bandwidth (resolution) of the x-ray source is inconsequential. In principle, white (a broad, smooth continuum of energy), pink (an unfiltered undulator beam with energy band path of hundreds of electronvolts), and monochromatic (a narrow, electronvolt band path of photon) x-rays can all be used as the source.

Examples of high-pressure XES include the study of predicted high-spin/low-spin transitions in iron oxides and sulfides. A schematic of the K_{β} emission process in Fe^{2+} is shown in Figures 10 and 11. In an atomic picture, the final state of the K_{β} is a whole state with $1s^2 3p^5 3d^5$. The measurement also reveals the XANES portion of the spectra, that is, including the pre-edge peak associated with transitions to unoccupied d-states (i.e., 3d in Fe). By measuring the absorption through selective monitoring of the fluorescence peaks, information on the contribution of different spins to the spectrum can be obtained.

XES of the $\text{Fe-}K_{\beta}$ emission was first measured with a white x-ray source at a second-generation facility (NSLS); the high-spin to low-spin transition in troilite (FeS), coinciding with its I–II structural transition, was observed (Rueff et al., 1999). Subsequently, with higher source intensity, the technique has

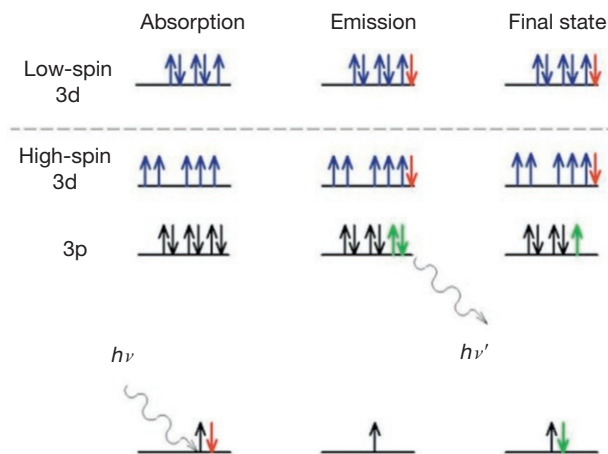


Figure 10 The schematic diagram of the K_{β} emission process.

been applied at APS and European Synchrotron Radiation Facility (ESRF) for studies of high-spin to low-spin transitions in wüstite (Badro et al., 1999), hematite (Badro et al., 2002), magnesiowüstite (Badro et al., 2003), perovskite (Li et al., 2004; Lin et al., 2012), and postperovskite (Yamanaka et al., 2012) to above 100 GPa pressures. The technique has been extended to high P – T conditions in combination with laser-heating techniques (Figure 12).

Resonant XES (RXES), or partial fluorescence yield (PFY), has also been successfully utilized in high-pressure studies. RXES may be viewed as a combination of XES and XAS. Instead of collecting transmitted x-rays as in XAS, emission spectra are measured at each step as the incident beam energy is changed or scanned across an absorption edge. This resonant method significantly enhances footprints of electron states and has a remarkable sharpening effect in projected spectra (RXES or PFY) (Rueff, 2010; Wang et al., 2010). Resonant x-ray emission spectra have allowed for resolving crystal field splitting of Fe^{3+} in Fe_2O_3 at HP (Wang et al., 2010) and intermediate-spin state of Fe_3O_4 at 15–16 GPa (Ding et al., 2008).

There have been significant developments in the ab initio treatment of such spectra, in particular, the electron–hole attraction, which requires going beyond a simple mean-field approach such as the local-density approximation (LDA) (Shirley, 1998). This is needed for x-ray absorption and RIXS. Measurements of the effect of pressure on plasmon excitations in metals (e.g., the high-pressure phase of Ge) suggest the potential for investigating the electronic structure of core materials at megabar pressures.

2.13.4.4.3 x-Ray inelastic near-edge spectroscopy

Near core-electron absorption edge features measured by soft x-ray absorption (XANES) or electron energy loss spectroscopy reveal information on chemical bonding. Such information is particularly pronounced and important for light elements but has been inaccessible for high-pressure studies as the pressure vessel completely blocks the soft x-ray and electron beams. With XINES, the high-energy incident x-ray penetrates the pressure vessel and reaches the sample. The scattered photon loses a portion of energy corresponding to the K-edge of the low-Z sample but can still exit the vessel to be registered on

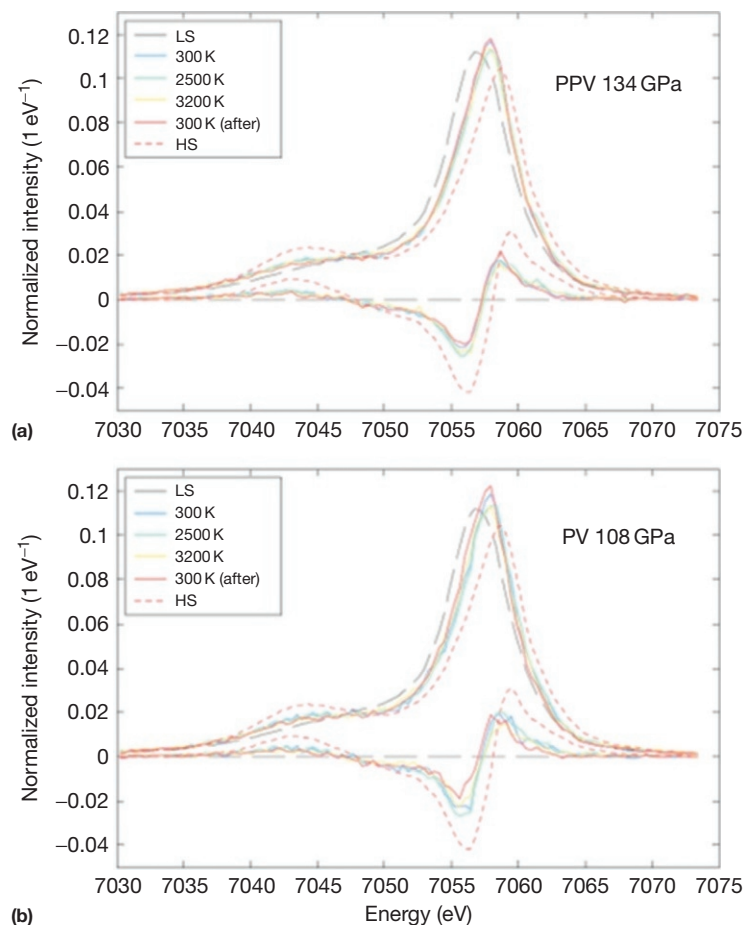


Figure 11 x-Ray emission spectra of (Mg,Fe)SiO₃ postperovskite at 134 GPa and perovskite at 108 GPa in laser-heated DAC. High-spin and low-spin references are used for the integrated absolute difference analysis, and differences from the low-spin line shape, shown below the spectra, are used to derive the average spin number of Fe²⁺. An energy shift of 0.8 eV in the main K_{β} emission peak, which is approximately half of the energy shift in the high-spin to low-spin transition in ferropericlase, is also used to derive the total spin number, providing an additional evidence for the occurrence of the intermediate-spin state. Reproduced from Lin JF, Watson H, Vanko G, et al. (2008) *Nature Geoscience* 1: 688–691.

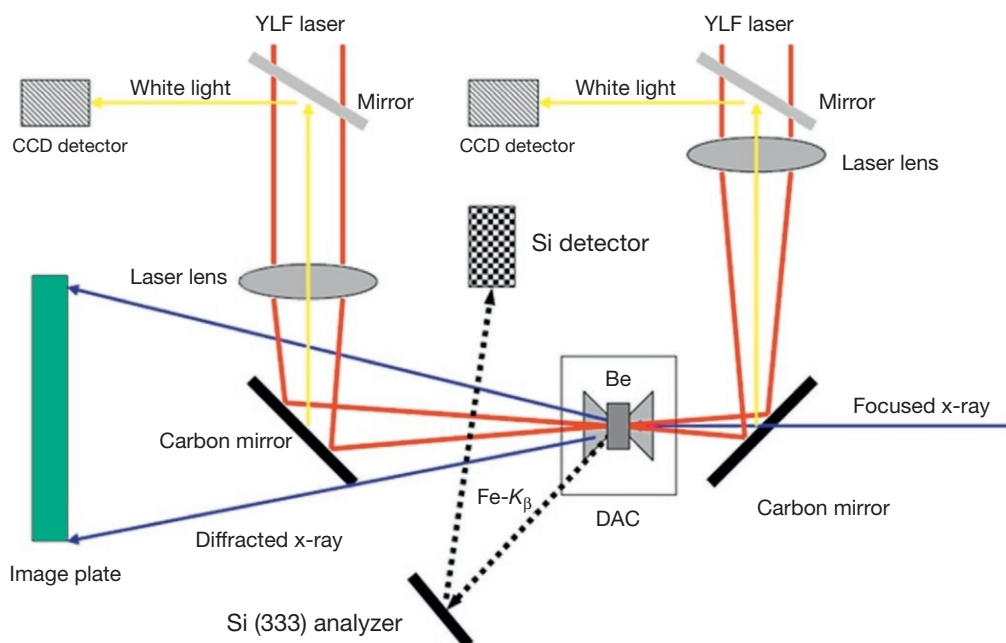


Figure 12 Schematic of the x-ray emission spectroscopy with laser-heated DACs. The YLF laser beam is focused to 25 μm onto the both sides of the sample surfaces. The diameter of the focused x-ray beam at 14 keV was approximately 7 μm (FWHM); the small beam size ensures that the x-ray emission signal from the sample is measured only within the laser-heated spot of 25 μm . The technique has been used to the study single-crystal magnesiowüstite [(Mg_{0.76}Fe_{0.24})O] sample loaded into the sample chamber of a diamond anvil cell with flat diamonds with a culet size of 300 μm . The Fe- K_{β} fluorescence lines were collected through the Be gasket by an 1 m Rowland circle spectrometer in the vertical scattering geometry. An image plate (MAR345) is used to collect diffracted x-ray in the forward direction. Figure reproduced from Lin JF, Struzkhin VV, Jacobsen SD, et al. (2005d) *Journal of Synchrotron Radiation* 12: 637–641.

the analyzer–detector system. Inelastic K-edge scattering spectra of second-row elements from Li (56 eV) to O (543 eV) at high pressures opened a wide new field of near K-edge spectroscopy of the second-row elements, as in carbon in graphite (Lin et al., 2011; Mao et al., 2003a) and boron and oxygen in amorphous Earth materials (Lee et al., 2014).

In XINES experiments, spherically bent single-crystal analyzers collect scattered x-radiation and focus it to the detector at nearly backscattering geometry, thus fixing the energy at the elastic line. The incident x-ray energy is scanned relative to the elastic line to determine the inelastic (Raman) shift. Since XINES probes the core-electron energy level at hundreds of electronvolts, the undulator gap need to be changed to follow the energy scan of the double monochromator. For most high-pressure XINES measurements, the intrinsic peak width is of the order of electronvolts, and the direct beam without a high-resolution monochromator and 1 m analyzer-to-detector distance would usually suffice. The angle 2θ between the incident beam and the scattered x-radiation defines the momentum transfer ($q = 4\pi E \sin \theta$ where E is the scattered x-ray energy). XINES features are relatively insensitive to q , except for the extremely large and small q (Krisch et al., 1997). The 2θ angle for high-pressure XINES study can thus be set at an angle (e.g., 30°) to optimize the intensity, the collimation in the detection path, and multiple analyzers used to increase the count rate without discriminating q . Data collection efficiency can be increased by the use of an array of analyzers developed; such techniques were used for measurements for graphite (Lin et al., 2011; Mao et al., 2003a), boron (Lee et al., 2008a; Meng et al., 2004), hydrocarbons (Fister et al., 2007), oxygen in glasses (SiO_2 , B_2O_3 , GeO_2 , and MgSiO_3) (Lee et al., 2008a; Lelong et al., 2012; Lin et al., 2007; Yi and Lee, 2012), and H_2O (Cai et al., 2005; Fister et al., 2009). Because the features in XINES are sensitive to local ‘short-range’ structure, the technique has been particularly useful in revealing structural changes in no-crystalline oxides and silicates at high pressure. For example, topological disorder tends to increase with pressure as shown by the increase in the width of the O K-edge absorption with increasing pressure (Lee et al., 2008b). The XINES data of shock-compressed oxide glasses provide strong geochemical implications for impact processes (Lee et al., 2012).

2.13.4.4.4 x-Ray magnetic circular dichroism

This technique measures the spin polarization of an electronic excitation on FM materials by the use of circularly polarized x-rays. It is therefore in principle identical to conventional optical magnetic circular dichroism (MCD) with visible light (magneto-optic Kerr effect). In synchrotron radiation experiments, an x-ray phase plate changes the x-rays from linearly to circularly polarized. XMCD can be observed in both XANES and EXAFS. XMCD in XANES can measure spin-resolved conduction band densities of states, whereas XMCD in EXAFS provides local magnetic structural information. The sign of the dichroism gives the FM coupling between atoms in a metal. High-pressure MCD measurements have been performed (Baudalet et al., 1997). For magnetic samples, magnetic circular dichroism is also observable in XES by exciting core holes with circularly polarized x-rays. With the low end of the high-energy window extended down to 4 keV by the high-strength Be gasket, all elements above Ca ($Z = 20$) in principle

can be studied at high pressure with a suitable choice of analyzer crystals. Crystal analyzers have been developed for inelastic x-ray scattering (IXS) with subelectronvolt energy resolution of emission spectral line shapes for studies of oxidation states, electronic energy level, spin states, and trace element analysis. In particular, the important 3d and 4f emission bands can be studied to very high pressures (Fabbris et al., 2013; Gorria et al., 2009; Haskel et al., 2011; Iota et al., 2007; Souza-Neto et al., 2012).

XMCD is the technique of choice to study ferro(ferri)magnetic materials, yielding element and orbital-selective magnetization, which is of advantage in cases where more than one magnetic element is present. The selectivity is also beneficial for elucidating the role of selected electronic orbitals in mediating magnetic interactions. Neutron scattering techniques, on the other hand, probe the magnetic moment of all scattering atoms simultaneously. Similarly, SQUID magnetometry lacks element specificity and is limited to lower applied pressures due to restrictions in sample environment. Other x-ray probes of magnetism include XES and nuclear resonance x-ray scattering (Mössbauer) spectroscopy. Unlike XMCD, XES is a probe of local magnetic moment and is not sensitive to magnetic ordering, while Mössbauer spectroscopy can only be applied to selected isotopes.

2.13.4.4.5 Electronic inelastic x-ray scattering

Pressure has dramatic effects on the energy and dispersion of all electronic bands. Many electronic levels, including some of the most intriguing pressure-induced changes, occur above the intrinsic, 5 eV, bandgap of the diamond window and are thus inaccessible by the standard vacuum techniques such as electron and ultraviolet spectroscopy probes. Using 10 keV x-ray beam for excitation and 0.3–1 eV resolution, IXS can in principle probe the full range of high-energy electronic levels, that is, the electronic band structure (Caliebe et al., 2000), Fermi surface (Huotari et al., 2000), excitons (Arms et al., 2001; Mao et al., 2010), plasmons (Hill et al., 1996; Mao et al., 2011), and their dispersion at high pressure. The instrumentation of EIXS is similar to that of XINES, except both energy and q need to be scanned to obtain the dielectric function $\epsilon(E, q)$ and the dynamic structure factor $S(E, q)$, EIXS probe valence, and conduction electronic structures at low energies up to a few tens of electronvolts from the elastic line. Many high-pressure EIXS can use the same 1 eV resolution setup as high-pressure XINES.

2.13.4.4.6 Resonant inelastic x-ray spectroscopy

Shallow core excitations are the same excitations probed by soft XAS and are rich in multiplet structures for these highly correlated electronic systems. There have been a growing number of RIXS studies of core excitations (Ament et al., 2011; Bartolome et al., 1997; Hill et al., 1998; Kao et al., 1996a; Kotani and Shin, 2001; Krisch et al., 1995; Rueff, 2010); that is, the final states of the inelastic scattering process in these studies are localized shallow core excitations. For magnetic samples, excitation with circularly polarized x-rays can also provide information on spin-resolved electronic structure (DeGroot et al., 1997; Krisch et al., 1996).

In RIXS experiments, both incident and scattered x-ray energies are scanned. The incident x-ray energy is scanned

across the core absorption similar to the procedures for XAS. For each monochromatic incident x-ray energy, fluorescence spectra are collected by scanning analyzers similar to the procedures of XES. One can obtain selected information connected directly with a specific intermediate state to which the incident photon energy is tuned. RIXS in transition metal and rare earth systems gives us important information on the electronic states, such as the intra-atomic multiplet coupling, electron correlation, and interatomic hybridization. Unusual phase transitions driven by electron correlation effects occur in many transition metals and transition metal compounds at high pressures, some accompanied with large volume collapses (e.g., 5–17% in rare earth metals and 10–15% in magnetic 3d transition metal oxides) (Bradley et al., 2012). Examples include Bradley et al. (2012), Maddox et al. (2006), and Ding et al. (2008). The nature of these transitions, including the relationships between the crystal and electronic structures and the role of magnetic moment and order, is an area of active study (e.g., Ament et al., 2011).

2.13.4.4.7 IXS spectroscopy

IXS spectroscopy (IXSS) measures the dynamical structure factor, and as such, it is similar to inelastic neutron scattering (Ghose, 1988). Formally, $S(q, \omega)$ is related to the space-time Fourier transform of the density correlation function, which provides information on the electronic band structure and elementary excitations (such as phonons and plasmons) and in turn thermal, optical, magnetic, and transport properties of the material (Ament et al., 2011; Hill et al., 1996). IXSS has a number of advantages in comparison with other scattering probes, such as those that use (optical) light, electrons, and neutrons (Kao et al., 1996b; Krisch et al., 1995). For example, light scattering can only probe zero-momentum transfer transitions; electron scattering suffers from multiple scattering effects and can only be used in high vacuum conditions; neutron scattering needs very large samples. On the other hand, IXSS covers wide length (momentum) and temporal (energy) scales that are potentially important in high-pressure mineral studies. Low-energy excitations have been studied with ultra-high resolution (~ 1.5 meV or 12 cm $^{-1}$) IXSS techniques (Ruocco et al., 1996; Sampoli et al., 1997). The resolution that can be achieved is as good as or better than what has been achieved by the best angle-resolved photoemission spectrometer.

Another variation on these techniques is high-resolution resonant x-ray Raman scattering, which is in principle like the more familiar Raman scattering at optical wavelengths. It can be viewed as an instantaneous absorption and emission process where the initial and final states are electronic and magnetic (rather than vibrational) states. In such RIXS, one detects electronic excitations of $\omega = \omega_1 - \omega_2$ and monitors momentum transfer $q = q_1 - q_2$. Examples include the study of the metal-AFM insulator transitions (Isaacs et al., 1996), but the technique has not yet been used for high-pressure minerals. Studies at ambient pressure have shown that it is possible to measuring EXAFS-like spectra for K-edges of low-Z elements by x-ray Raman; similar studies in high-pressure cells could provide probes of local structure (e.g., of Si) that cannot be studied by direct EXAFS techniques.

2.13.4.4.8 Compton scattering

CS is an inelastic scattering at high momentum transfer that probes electron momentum distributions. The details of the momentum distribution reveal information about bonding type (e.g., covalency) and band structure, particularly in combination with electronic structure theory (Isaacs et al., 1999). The availability of intense synchrotron radiation sources, particularly the high brightness at very high energies (~ 50 keV), and the development of high-resolution spectrometers are opening up new classes of CS experiments on small samples and at high pressures. The method has been applied to elemental solids such as Na and Si in Paris-Edinburgh cells, but not yet to geophysical materials (Hämäläinen et al., 2000; Tse et al., 2005).

2.13.4.4.9 Nuclear resonance forward scattering

As described earlier in the text, Mössbauer spectroscopy has been used extensively in high-pressure mineralogy in laboratory studies with a radioactive parent source. High-pressure studies using a conventional Mössbauer source suffer from limited intensity for measurements on small samples, absorption by anvils, and background scattering. There have been major advances that exploit the temporal structure of synchrotron radiation to perform nuclear resonance spectroscopy in the time domain (Hastings et al., 1991; Sturhahn, 2004). With this technique, highly monochromatized x-rays from the synchrotron are used to excite narrow nuclear resonances, and the delayed photons are detected (Figure 13). Hyperfine splittings are reconstructed from the time-dependent intensity. The phonon densities of states around the nuclei can also be measured. Mössbauer spectroscopy has been used successfully to study Fe and Eu at second-generation synchrotron sources (Chefki et al., 1998; Nasu, 1996; Takano et al., 1991). The NRFS technique has been extended to probe magnetism up to megabar pressures (Figure 14).

Because of the high brilliance and highly focused beam, NRFS is well suited for, and has been extensively used in, high-pressure research of deep Earth materials. The NRFS hyperfine signals are very sensitive to internal magnetic fields, electric field gradients, and isomer shifts and are widely used in recent years to study magnetic collapse (Li et al., 2004; Lin et al., 2005b), site occupancy (Catalli et al., 2011; Lin et al., 2012), and valence and spin states (Chen et al., 2012; Jackson et al., 2005b; Shim et al., 2009; Speziale et al., 2005). Compared with other nuclear resonant techniques, NRFS measures the transmission signals that are relatively strong and may be collected in a fast manner. For example, fast NRFS experiments have been performed to determine high-pressure melting temperatures of iron by measuring the Lamb-Mössbauer factor, which describes the probability of recoilless absorption (Jackson et al., 2013).

2.13.4.4.10 Nuclear resonant inelastic x-ray scattering

Nuclear resonant scattering yields information on the phonon DOS through an inelastic scattering process (Figure 13). In principle, the DOS provides constraints on dynamic, thermodynamic, and elastic information of a material, including vibrational kinetic energy, zero-point vibrational energy, vibrational entropy, vibrational heat capacity, Debye temperature, Grüneisen parameter, thermal expansivity, longitudinal velocity, shear velocities, bulk modulus, and shear modulus. By

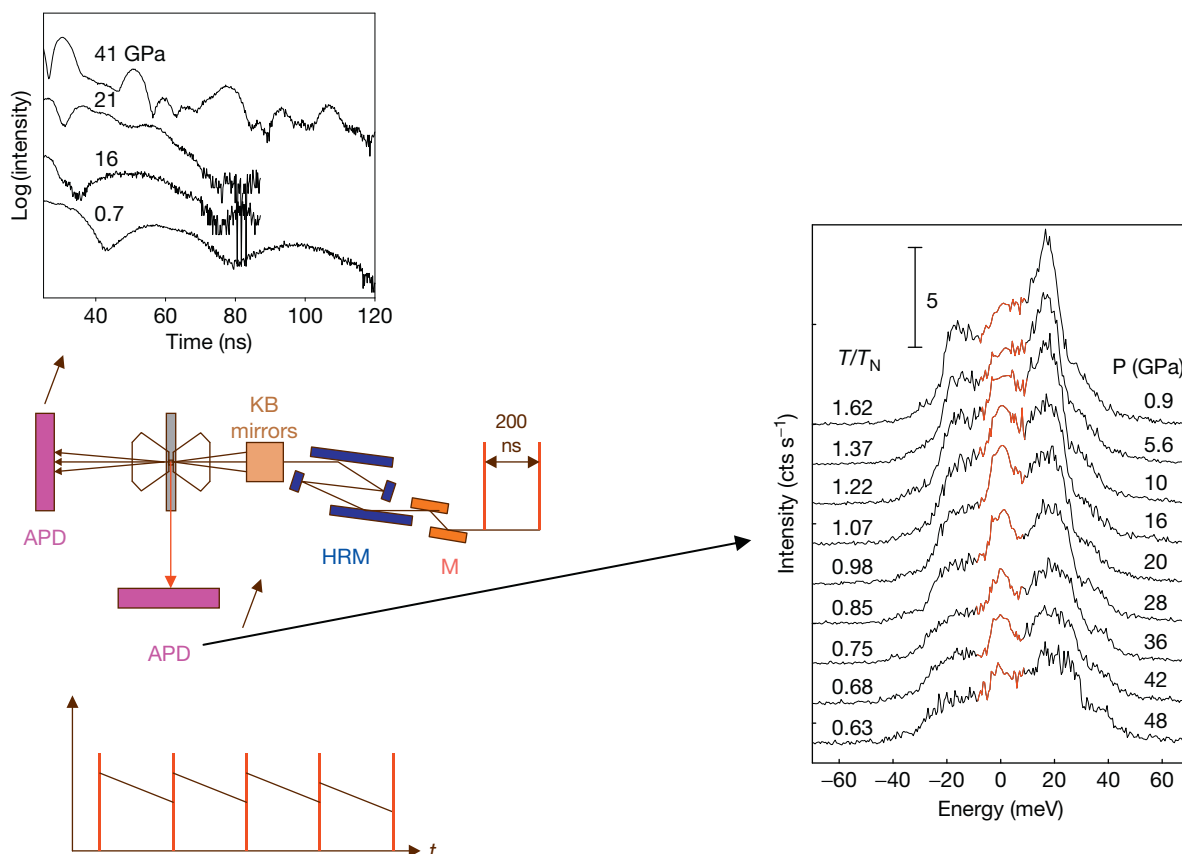


Figure 13 High-pressure nuclear resonant inelastic x-ray scattering. In-line high-resolution monochromator used to narrow down the photon energy to millielectronvolt resolution and fine-tune the monochromatic x-ray near the narrow nuclear resonant (elastic) line. Avalanche photodiodes (APDs) are used to collect only signals from nuclear resonance absorption and reject all nonresonantly scattered radiation. An APD directly downstream of the sample collects nuclear forward scattering and the APDs surrounding the sample collect nuclear resonant inelastic x-ray scattering (NRIXS) spectroscopy (Hu et al., 2003; Sturhahn et al., 1995). Nuclear resonant forward scattering spectra of FeO (top) and NRIXS spectra of FeO (right) through the pressure-driven transition from the paramagnetic (NaCl structure) to the antiferromagnetic (AFM) (rhombohedral structure) phase above 17 GPa. Reproduced from Struzhkin VV, Mao HK, Hu J, et al. (2001) *Physical Review Letters* 87: 255501.

using time discrimination electronics, the delayed signals caused by the narrow nuclear absorption provide NRIXS data (Sturhahn, 2004). Measurements were first carried out on ^{57}Fe in its bcc metallic iron at ambient conditions (Seto et al., 1995; Sturhahn et al., 1995). The NRIXS technique has been extended to high pressure and obtained the DOS of ϵ -Fe up to 153 GPa (Mao et al., 2001) and as a function of pressure and temperature with laser-heating techniques (Lin et al., 2005; Zhao et al., 2004). The measurement of the Debye sound velocity (Murphy et al., 2011; Wicks et al., 2010) distinguishes compression and shear wave velocities and their temperature and pressure dependence. This technique also allows the determination of anisotropy of sound velocities and mode Grüneisen constants (Murphy et al., 2011). High-pressure studies have been carried out on iron (Gleason and Mao, 2013; Lin et al., 2005b; Mao et al., 2001), (Mg,Fe)O (Chen et al., 2012; Struzhkin et al., 2001); Fe-Ni, Fe-C, and Fe-Si alloys (Lin et al., 2003b; Mao et al., 2012); (Mg,Fe)SiO₃ glass (Gu et al., 2012); (Mg,Fe)SiO₃ enstatite (Jackson et al., 2009a); (Mg,Fe)SiO₃ perovskite (Catalli et al., 2011); and (Mg,Fe)SiO₃ post-perovskite (Catalli et al., 2010; Jackson et al., 2009b).

2.13.4.4.11 Phonon inelastic x-ray scattering

PIXS is used for studying lattice dynamics. Because nonresonant PIXS requires high-energy resolution (meV) and the double differential scattering cross section of phonon IXS is very small, such an experiment is very demanding even with the brilliance of third-generation synchrotron undulator sources. Additional challenges posed by high-pressure studies are limitations in sample size. Nonresonant PIXS has been applied to studying the high-pressure elasticity anisotropy of ϵ -Fe and of d- and f-electron metals (Manley et al., 2003; Wong et al., 2003). Sound velocities of materials to over 1 Mbar have been measured (Antonangeli et al., 2010, 2011; Fiquet et al., 2001) using this technique. With single-crystal samples, complete phonon dispersions in the Brillouin zone may be mapped by PIXS at high pressures (Farber et al., 2006). However, lattice dynamical data at high pressure are still limited, largely due to constraints by the strict requirements of sample quality, hydrostaticity, and, to some extent, beam time availability.

Recently, a compact laser-heated DAC has been integrated with the PIXS technique (Fukui et al., 2013). Sound velocities of iron and iron alloys have been measured at high pressure

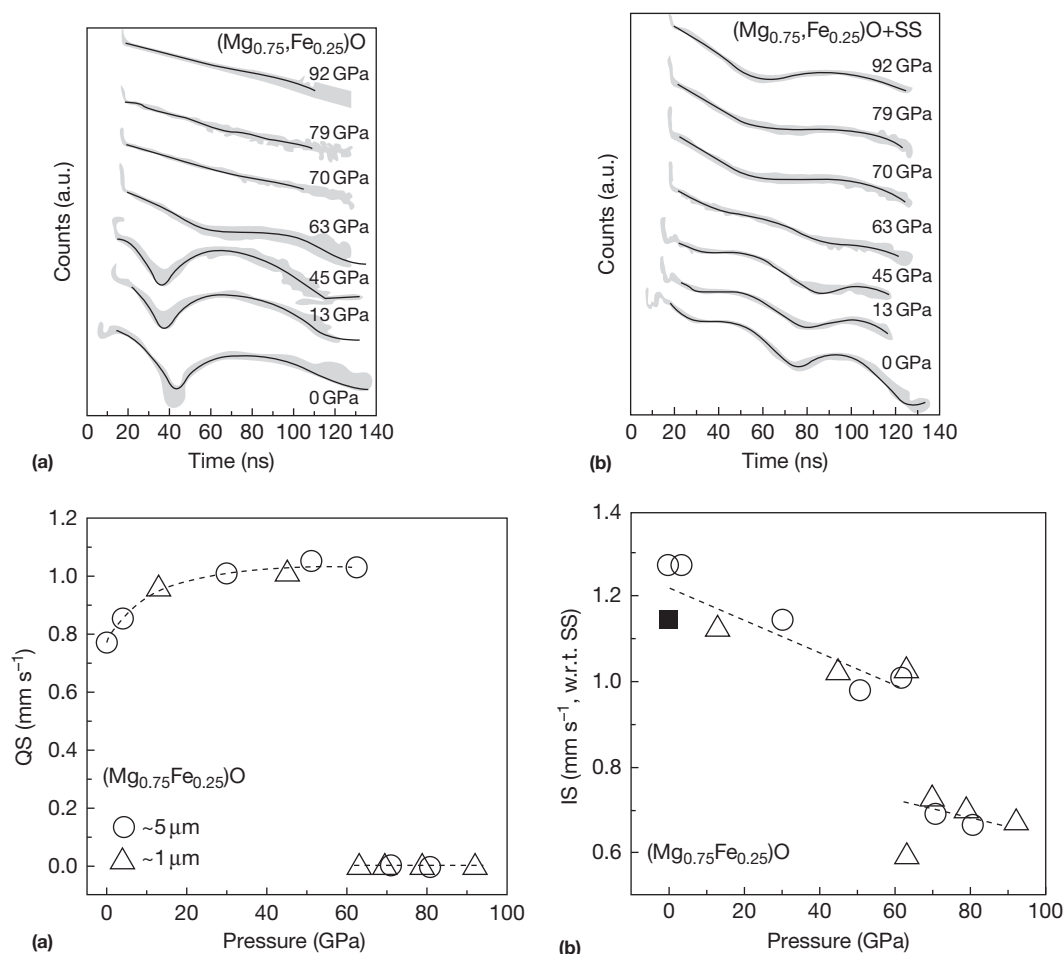


Figure 14 Representative nuclear resonant forward scattering (NRFS) spectra. Top: $(\text{Mg}_{0.75}\text{Fe}_{0.25})\text{O}$ (a) and $(\text{Mg}_{0.75}\text{Fe}_{0.25})\text{O}$ with stainless steel (b) as a function of pressure at room temperature. Black line, modeled spectrum with the MOTIF (Shvyd'ko, 1999) program. The sample thickness was approximately $1 \mu\text{m}$, and the stainless steel foil of $\sim 0.5 \mu\text{m}$ was used outside the diamond anvil cell to generate quantum bits in synchrotron Mössbauer spectra (SMS) spectra for isomer shift (IS) measurements. Evolution of the NRFS spectra of $(\text{Mg}_{0.75}\text{Fe}_{0.25})\text{O}$ with the stainless steel as a reference enables derivation of the IS of the sample as a function of pressure. The quantum bits at 0, 13, and 45 GPa generated from the quadrupole splitting (QS) of the high-spin state of iron in the sample, whereas the flat feature of the spectra at 70, 79, and 92 GPa indicates disappearance of the QS. The spectrum at 63 GPa is modeled with two states, a state with a QS and a state with QS, which may explain the pressure gradient in the sample chamber. Bottom: pressure dependence of (a) QS and in $\text{Mg}_{0.75}\text{Fe}_{0.25}\text{O}$ as revealed from the modeling of the NRFS spectra. The disappearance of the QS and the significant drop of the IS at above 63 GPa are consistent with the high-spin to low-spin electronic transition of iron in the sample occurring between 51 and 70 GPa. A least-squares fit to the IS (short dashed lines) gives $d(\text{IS})/dP$ of $-0.0037 (\pm 0.0007) \text{ mm s}^{-1} \text{ GPa}^{-1}$ for the high-spin state and $d(\text{IS})/dP$ of $-0.0021 (\pm 0.0010) \text{ mm s}^{-1} \text{ GPa}^{-1}$ for the low-spin state, respectively. At 63 GPa, modeling of the NRFS spectrum indicates coexistence of two states, high-spin state and low-spin state of Fe^{2+} .

and high-temperatures conditions (Kamada et al., 2014; Ohtani et al., 2013; Shibasaki et al., 2012).

2.13.4.5 Transport Measurements

2.13.4.5.1 Electrical conductivity

Electrical conductivity has been measured under pressure in a wide variety of apparatus since the pioneering work of Bridgman (1949). The principal technique is the four-probe method. The method has been used in multianvil presses for studies of upper and lower mantle minerals, including studies of the $(\text{Mg,Fe})\text{SiO}_4$ polymorphs of the upper mantle (Xu et al., 1998a) and $(\text{Mg,Fe})\text{SiO}_3$ perovskite (Xu et al., 1998b). The method has also been extensively applied in diamond anvil

cells that provide the opportunity to access higher pressures (Mao and Bell, 1981). A modified pseudo-four-probe technique has been applied at megabar pressures (see Hemley et al., 2002). The technique has been extended to above 200 GPa at room temperature down to 0.05 K (Eremets et al., 1998). The technique was early on used in conjunction with high P - T laser heating (e.g., Li and Jeanloz, 1987) and resistive heating (e.g., Peyronneau and Poirier, 1989).

A large number of studies of conductivity of Earth materials have now been done in the diamond anvil cell. Gomi et al. measured conductivity of hcp iron to 100 GPa at room temperature (Gomi et al., 2013). Conductivities of perovskite, postperovskite, and bulk mantle compositions have also been measured (Ohta et al., 2008, 2010a,b).

Micro lithographic techniques are allowing still smaller leads to be attached to or actually built into the surface of the anvils for achieving both higher pressure and higher accuracy. The technique can also be coupled with a radiation field for carrying out photoconductivity measurements under pressure. Extensions of these techniques are benefiting from the development of designer anvil methods (Patterson et al., 2000, 2004).

The multianvil experiments mentioned in the preceding text used a complex impedance method commonly used at ambient pressure (Poe et al., 1998). In this technique, the frequency of the current is varied over a wide range (from 0.01 Hz to 1 MHz); measurements on $(\text{Mg,Fe})_2\text{SiO}_4$ polymorphs to 20 GPa as a function of temperature indicate that the conductivity in the high-pressure phases (wadsleyite and ringwoodite) is a factor of 10^2 higher than that in olivine (Poe et al., 1998), consistent with previous low-pressure studies. Another useful example is conductivity measured along the Hugoniot in shock-wave experiments (Knittle et al., 1986), including the more recent reverberation approach (Weir et al., 1996).

2.13.4.5.2 Magnetic susceptibility

The magnetic susceptibility χ describes the response of a system to an applied magnetic field. Diamagnetic materials have negative χ . Paramagnetic and FM materials have positive χ . For paramagnetic materials, $\chi \sim 10^{-6}$ – $10^{-5} \text{ m}^3 \text{ G}^{-1}$, and for FM materials, χ is several orders of magnitude higher. Typically, one reports the differential magnetic susceptibility, $\chi_x = d\chi/dH$. For example, $\chi_x = 1100$ for Fe at external magnetic field $H = 0$. Several classes of high-pressure techniques have been developed. One involves measurement with SQUIDs (Webb et al., 1976). A second is an inductive technique developed by Tissen and Ponyatovskii (1987) and later extended by Timofeev (1992). Originally applied to study superconductivity under pressure, it has been extended to investigate other pressure-induced magnetic transitions, including those in Fe (Timofeev et al., 2002; Figure 15). The designer anvil technique continues to be used for studies of magnetic transitions, for example, in FM rare earth materials (Jackson et al., 2005a). More recently, these methods have been extended with the use of focused ion beam techniques for precise lithography of diamond anvil cells

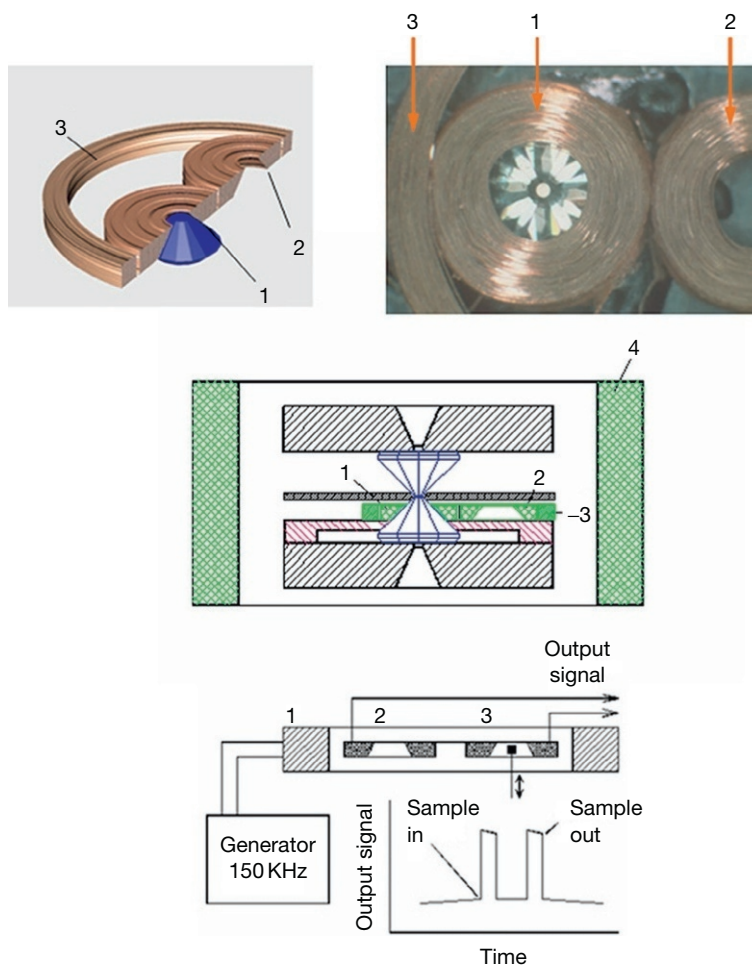


Figure 15 High-pressure magnetic susceptibility technique. Top: double-frequency modulation setup – coil 4 is used to apply low-frequency magnetic field to modulate the amplitude response from the high-frequency pickup coil 2 due to the superconducting sample. The setup includes two signal generators and two lock-in amplifiers, operating at low (20–40 Hz) and high (155 KHz) frequencies. Bottom: schematic representation of the background subtraction principle in magnetic susceptibility measurements – 1, primary coil; 2, secondary compensating coil; 3, secondary signal coil. Removal of the sample from the signal coil produces measurable changes in the total output signal.

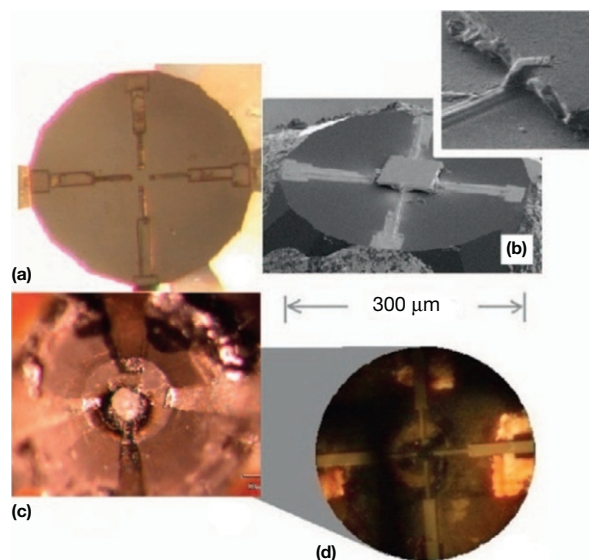


Figure 16 Anvils with an electrical probe assembly. (a) The flat diamond culet with the probes produced with a focused ion beam (FIB) before the attachment of the sample. (b) The same diamond with the sample attached. The inset shows one probe running over the edge of the crystal sample. (c) The Pt metal leads inside the indented boron nitride (BN) that will carry the signal from the sample to FIB electrical probes further to the electronics. (d) The culet after closure of the DAC with the attached sample and FIB probes in contact with the outer Pt-foil leads. Reproduced from Rotundu C, Cuk T, Greene RL, Shen ZX, Hemley RJ, and Struzhkin VV (2013) *Review of Scientific Instruments* 84: 063903.

and samples, with experiments performed in inert gas pressure media (Rotundu et al., 2013; Figure 16).

2.13.4.6 Resonance Methods

2.13.4.6.1 Electron paramagnetic and electron spin resonance

Various techniques have been developed for electron paramagnetic resonance (EPR) and electron spin resonance (ESR), which involves resonant microwave absorption between spin levels split in a magnetic field (the Zeeman effect). This requires coupling of the microwave field, with the sample, which can be challenging at high pressure because of the small sample size (dimensions less than the wavelength of the radiation; Figure 17). Studies to ~ 8 GPa have been reported. Measurements on mantle silicates have been carried out at ambient pressures (e.g., Sur and Cooney, 1989).

2.13.4.6.2 Nuclear magnetic resonance

Nuclear magnetic resonance (NMR) is similar to EPR in that it too involves splitting of magnetic levels (Kirkpatrick, 1988; Stebbins, 1988). Because the magnetic moments of the nuclei are three orders of magnitude smaller than that of the electron, the level splitting is much lower in energy (radio-frequency range, or ~ 100 MHz) at typical laboratory magnetic fields ($H \sim 5\text{--}10$ T). NMR studies of high-pressure phases recovered at zero pressure include ^1H and ^{29}Si NMR studies of quenched high-pressure hydrous phase (Phillips et al., 1997) and magic angle spinning ^{29}Si relaxation techniques for characterizing naturally shocked samples (e.g., silica phases from Coconino Sandstone) (Meyers

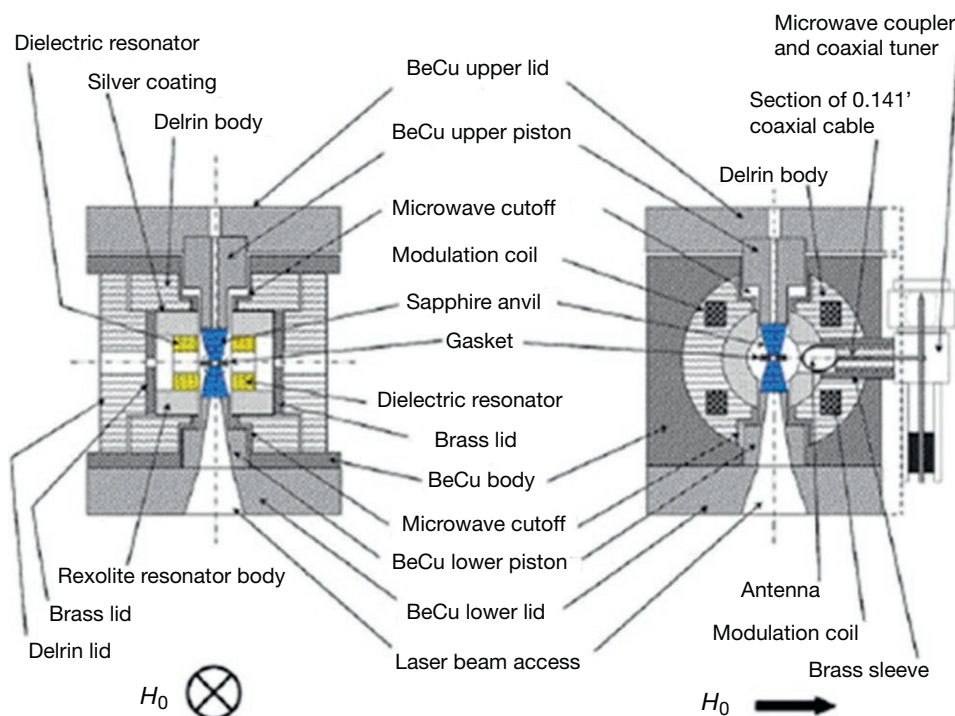


Figure 17 Cross-sectional view of the high-pressure electron spin resonance probe including the microwave coupler and coaxial tuner (see Sienkiewicz et al. (2005) for further details).

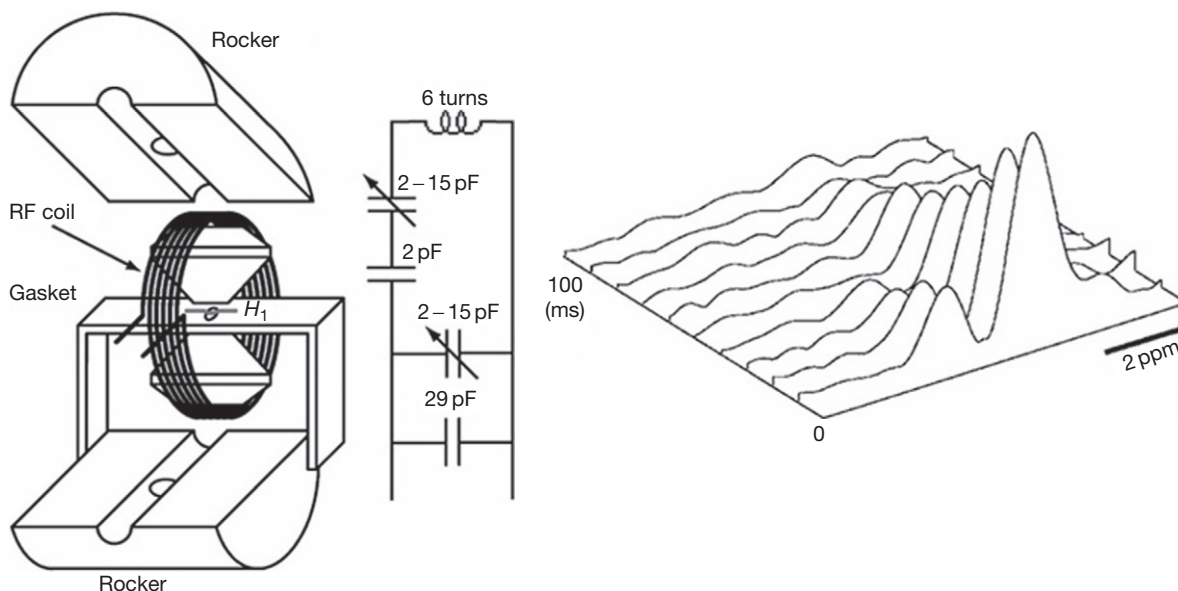


Figure 18 Technique for in situ nuclear magnetic resonance (NMR) in DACs (Okuchi et al., 2005a). Left: schematic illustration of the single-solenoid r.f. probe and its circuit. Right: magnetization of CH_3OH observed at 2.7 GPa.

et al., 1998). The technique has been applied to investigate glasses under pressure (Poe et al., 1993; Yarger et al., 1995). Most recently, two-dimensional NMR experiments applied to pressure-quenched glasses reveal details of the changes in bonding associated with pressure densification (Lee et al., 2004, 2005).

There has been important progress in high-pressure NMR techniques (Figure 18). Proton NMR measurements have been carried out to 17 GPa (Pravica and Silvera, 1998a,b; Ulug et al., 1991). In situ high-pressure NMR measurements on H_2 , H_2O , and H_2O clathrates reveal information on the effect of compression on local bonding properties (e.g., H bonding) (Okuchi et al., 2005a,b,c). A related measurement is nuclear quadrupolar resonance, which is similar to NMR but consists of measuring nuclear resonances in zero field. Measurements of the quadrupolar resonance ^{63}Cu in Cu_2O have been performed to 6 GPa (Reyes et al., 1992). The numerous double-resonance techniques employed for years in condensed matter and chemical physics generally require larger sample volumes but potentially can be employed at high pressure with continued increases in sample size under pressure.

2.13.4.6.3 de Haas–van Alphen

This is a now standard technique for measuring Fermi surfaces of metals under ambient pressures, but it generally requires large, perfect single crystals. The advent of high-field magnets used in conjunction with new classes of diamond anvil cells offers the possibility of extending these measurements to high pressures. Again, such studies of iron alloys under pressure could provide important constraints on the evolution of fundamental electronic properties of core materials with pressures. Other extensions of magnetic susceptibility methods are described earlier in the text.

2.13.5 Selected Examples

We now discuss selected examples, focusing on systems where the combination of techniques discussed previously in the text

has been key to uncovering information on the electronic and magnetic properties of geophysically important materials.

2.13.5.1 Olivine

The electronic properties of $(\text{Mg,Fe})\text{SiO}_4$ olivine and its polymorphs can be considered a textbook problem in high-pressure mineral physics. In olivines, the bandgap varies from 7.8 eV in forsterite to 8.8 eV in fayalite (Nitsan and Shankland, 1976). A prominent excitonic absorption is observed near the bandgap (Nitsan and Shankland, 1976). Large changes in the optical absorption spectra under pressure were documented in the first in situ visible spectroscopy of minerals under pressure (Mao and Bell, 1972). As described earlier in the text, high-temperature measurements to 20 GPa indicate that the conductivity in the high-pressure phases (wadsleyite and ringwoodite) is a factor of 10^2 higher than that in olivine (Poe et al., 1998).

More recent work on olivine has included high P - T shock compression studies of olivine in which the optical absorption and emission spectra of the material have been used to constrain the emissivity and temperature on shock compression (Luo et al., 2004). The electrical conductivity of olivine containing 0.01–0.08 wt% water up to 1273 K and 4 GPa indicates that the conductivity is strongly dependent on water content and only modestly dependent on pressure and can be explained by the motion of free protons (Wang et al., 2006). Recent single-crystal measurements of electrical conductivity under pressure reveal a strong dependence on oxygen fugacity (Dai et al., 2006) and the mechanism of hydrogen incorporation and diffusion has been examined (Demouchy and Mackwell, 2006). The radiative heat transfer under pressure has been modeled based on high-pressure vibrational spectra (Hofmeister, 2005). These results have been complemented by subsequent laser flash measurements on olivine at zero pressure (Pertermann and Hofmeister, 2006).

The zero-pressure absorption edge of fayalite (Nitsan and Shankland, 1976) shifts from the UV to the near IR with pressure such that samples became opaque to visible light above 15–18 GPa; concomitantly, the electrical resistivity decreases by five orders of magnitude over this range (Lacam, 1983; Mao and Bell, 1972; Smith and Langer, 1982). A similar decrease in resistivity is also observed on shock-wave compression (Mashimo et al., 1980). The low-temperature AFM to paramagnetic transition has been tracked to at least 16 GPa by Mössbauer spectroscopy (Hayashi et al., 1987). First-principles calculations of the electronic structure and optical and magnetic properties of fayalite are consistent with the redshift of the absorption edge and decrease in electrical resistivity on compression (Jiang and Guo, 2004). Optical, electrical, and x-ray measurements extended to much higher pressures provided evidence that fayalite undergoes amorphization near 40 GPa with a further decrease in the bandgap (Williams et al., 1990).

2.13.5.2 Magnesio-wüstite

We consider the high-pressure behavior of magnesio-wüstite (Mg,Fe)O and its end-member phases MgO and FeO. Several examples of the changes in electronic and magnetic properties of these materials have been discussed already. Periclase (MgO) remains in the cubic rock-salt (B1) structure and remains electronically simple to at least 227 GPa (Duffy et al., 1995a), whereas wüstite (Fe_{1-x}O) exhibits complex polymorphism under pressure. Wüstite is nonstoichiometric and contains some ferric iron even in equilibrium with iron metal. The vacancies in wüstite form complex defect clusters (Hazen and Jeanloz, 1984). With increasing pressure, more stoichiometric wüstite can be stabilized. At room temperature and pressure, wüstite has the cubic rock salt (B1) structure. As temperature is lowered, it passes the Néel temperature T_N and becomes antiferromagnetically ordered and simultaneously assumes a distorted rhombohedral structure. As pressure is increased, T_N increases (Zou et al., 1980), so that pressure promotes the rhombohedral phase. Isaak et al. (1993) showed that pressure promotes the rhombohedral distortion even in the absence of magnetism. Theory reveals the origin of the rhombohedral distortion with pressure. Visualization of the charge density as a function of rhombohedral angle (Hemley and Cohen, 1996; Isaak et al., 1993) indicated that Fe–Fe bonding causes the rhombohedral strain, and the increase in Fe–Fe bonding with pressure is associated with the increased angle with pressure.

First-principles density functional theory (DFT) computations predicted that FeO and other transition metal monoxides would undergo magnetic collapse at high pressures (Cohen et al., 1997, 1998). Both LDA and the generalized gradient approximation give 100 GPa for a first-order high-spin to low-spin transition in AFM FeO for a cubic lattice with a 7–9% volume collapse and a continuous transition for FM cubic FeO (Cohen et al., 1998) and for rhombohedrally strained FeO (Cohen et al., 1997). The Mössbauer experiments show evidence for a transition at about 90 GPa to a low-spin phase and also a transition to a nonmagnetic phase with increasing temperature (Pasternak et al., 1997b), consistent with the DFT computations. On the other hand, XES shows no magnetic collapse up to 143 GPa and reinterprets the 90 GPa transition

observed by Mössbauer as a Néel transition (spin disordering) as opposed to magnetic collapse (Badro et al., 1999). LDA+U computations, which model local Coulomb repulsions not included in normal DFT calculations, predict high-spin behavior for AFM FeO to very high pressures (over 300 GPa), consistent with the XES measurements, but show metallization at lower pressures, depending on the value of U (Gramsch et al., 2003). A U of 4.6 eV, found by a self-consistent method (Pickett et al., 1998) and close to another recent estimate of 4.3 eV (Cococcioni and de Gironcoli, 2005), gives a pressure of only 60 GPa for metallization. (Gramsch et al., 2003); the lowest energy structure is predicted to be monoclinic (Gramsch et al., 2003) and was rediscovered by Cococcioni and de Gironcoli (2005). Neutron diffraction shows a monoclinic ground state at 10 K and zero pressure (Fjellvag et al., 2002), but single-crystal x-ray diffraction at high pressures has not resolved the monoclinic distortion (Jacobsen et al., 2005), perhaps because of the lack of high-angle data and/or twinning. LDA+U computations have now been performed for magnesio-wüstite (Persson et al., 2006; Tsuchiya et al., 2006), which show reasonable agreement with experiments. An analysis of high-spin to low-spin transitions from a crystal field perspective predicts a continuous magnetic collapse at high temperatures as a function of pressure (Sturhahn et al., 2005; Tsuchiya et al., 2006). However, when the PV term is included in the free energy, it is possible to obtain a different behavior (Persson et al., 2006), including possibly a first-order transition.

At high temperature, the transition originally identified by shock-wave experiments (Jeanloz and Ahrens, 1980) was found to be to a metallic phase (Knittle and Jeanloz, 1986), which was identified as the NiAs (B8) structure by in situ diffraction (Fei and Mao, 1994). The phase diagram indicates that it should occur at low temperatures as well. Subsequent analysis of the diffraction data suggested the formation of a polytype or superlattice between B8 and anti-B8, with Fe in the As-site and O in the Ni-site (Mazin et al., 1998). These B8 and anti-B8 structures can be joined together smoothly, and the boundary between them is the rhombohedrally distorted B1 structure. This phase could form due to lack of equilibrium or could even form a unique continuous structure transition between the different phases. This interpretation of the behavior of FeO has been confirmed by experiments (Kantor et al., 2004a; Murakami et al., 2004a,b). The phase diagram has been extended to higher P – T conditions and metallic B1 phase has been found (Ohta et al., 2012; Figure 19).

Recent studies of (Mg,Fe)O illustrate the importance of using multiple techniques. Theoretical studies indicate that the high-spin to low-spin transitions in a number of structures are dominated by the size of the local coordination polyhedron (Cohen et al., 1997). Thus, a transition metal ion in a smaller site will transform at lower pressures than one in a larger site. Thus, ferric iron in solid solution substituting for Mg^{2+} , which is a smaller ion than Fe^{2+} , transforms at lower pressures than in the pure ferrous iron compound. After being predicted theoretically, this has now been seen in a series of studies. XES shows a high-spin transition at 54–67 GPa in $(\text{Mg}_{0.75}\text{Fe}_{0.25})\text{O}$ and 84–102 GPa in $(\text{Mg}_{0.40}\text{Fe}_{0.60})\text{O}$, again suggesting that the transition in pure FeO is much greater than 100 GPa. Optical absorption spectra have been measured up to 80 GPa for the lower mantle oxide, (Mg,Fe)O. Upon

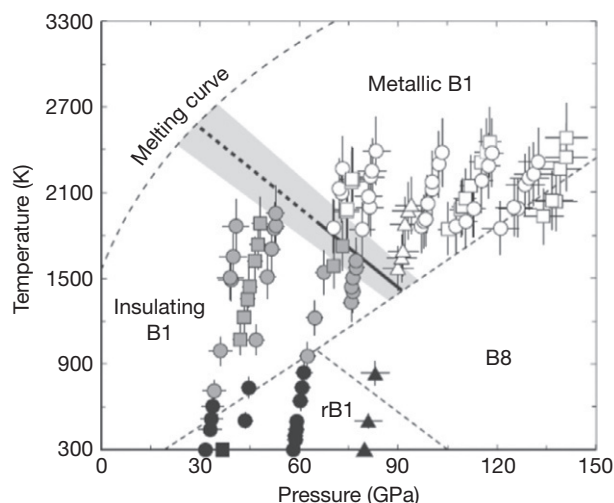


Figure 19 P - T phase diagram of FeO. The stability fields of rB1, insulating B1, and metallic B1 phases are represented by solid, gray solid, and open symbols, respectively. Circles, squares, and triangles indicate different sets of experiments. A metal-insulator transition boundary shown as bold line was determined from the data and linearly extrapolated to the melting condition (broken bold line). The estimated uncertainty in the location of the transition is shown by gray band. The melting curve and the phase boundaries of FeO shown as broken lines are from previous studies. Reproduced from Ohta K, Cohen RE, Hirose K, Haule K, Shimizu K, and Ohishi Y (2012) *Physical Review Letters* 108: 026403.

reaching the high-spin to low-spin transition of Fe^{2+} at about 60 GPa, there is enhanced absorption in the mid- and near-infrared spectral range, whereas absorption in the visible-ultraviolet is reduced. The observed changes in absorption are attributed to d-d-orbital charge transfer transitions in the Fe^{2+} ion (Figure 2). The results indicate that low-spin (Mg,Fe)O will exhibit considerably lower radiative thermal conductivity than the lower pressure high-spin (Mg,Fe)O (Goncharov et al., 2006). A schematic phase diagram is shown in Figure 20.

The Mössbauer data for high-pressure magnesiowüstite are less clear; they show hyperfine field split spectra coexisting with a paramagnetic peak over large pressure ranges (Speziale et al., 2005). The authors interpret the first appearance of a paramagnetic peak at the transition, but the data seem more consistent with coexisting high-spin and low-spin iron, perhaps in different local environments. In any case, these data are consistent with solid solution in which Mg^{2+} decreases the transition pressure, consistent with earlier predictions. Theory suggests that ferrous iron in the B8 or anti-B8 structures will remain high spin to much higher pressures. This also makes clear the distinction between magnetic collapse and metal-insulator transitions, since normal B8 FeO is predicted to be a high-spin metal and anti-B8 is predicted to be a high-spin insulator.

2.13.5.3 Silicate Perovskite and Postperovskite

The electronic properties of the silicate perovskite $(\text{Mg,Fe})\text{SiO}_3$ have been the focus of considerable study. UV-visible spectra indicate the presence of crystal field splitting (Shen et al., 1994), although subsequent measurements showed similar results for perovskite and magnesiowüstite (Keppler et al.,

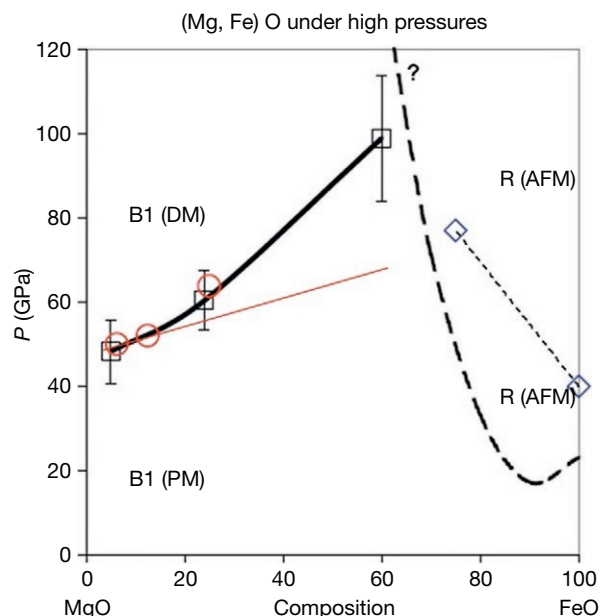


Figure 20 Phase diagram of the magnesiowüstite-(Mg,Fe)O system under high pressures. An isosymmetric transition from the paramagnetic state (PM) to the diamagnetic state (DM) occurs in MgO-rich magnesiowüstite (ferropericlase) (Badro et al., 2003; Lin et al., 2005b), and addition of FeO in MgO stabilizes the high-spin state to much higher pressures (Lin et al., 2005b). On the other hand, addition of MgO in FeO stabilizes the B1 structure relative to the AFM rhombohedral phase to much higher pressures (Lin et al., 2003c). Potential electronic and structural transitions in FeO-rich region remain to be further understood. Red-dashed line represents the calculated high-spin to low-spin transition boundary based on the assumption that the spin transition occurs at the same Fe-O bond length and the iron-iron exchange interaction could be neglected. Figure reproduced from Lin JF, Gavriluk AG, Struzhkin VV, et al. (2006) *Physical Review B* 73: 113107.

1994). A broad feature in the optical spectrum near $14\,900\text{ cm}^{-1}$ has been assigned to the $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ charge transfer transition (Keppler et al., 1994). Zhang (1997) measured the Lamb-Mössbauer factor on $(\text{Mg,Fe})\text{SiO}_3$ perovskites and clinoenstatite. The thermally activated electron delocalization found earlier in quenched samples in Mössbauer measurements with a conventional radioactive source (Fei et al., 1994) was suppressed at high pressure. Li and Jeanloz (1987) measured the electrical conductivity of $(\text{Mg,Fe})\text{SiO}_3$ perovskite at high pressures and temperatures by laser heating; subsequent measurements were carried out at lower maximum temperatures by Peyronneau and Poirier (1989) using a resistively heated cell. The latter results fit a hopping conductivity model. Katsura et al. (1998) reported that the temperature dependence of the conductivity differed significantly between samples measured at high pressure in its stability field and samples quenched to ambient pressure.

The strong partitioning of Fe^{2+} in magnesiowüstite relative to ferromagnesian silicate perovskite has been attributed to crystal field stabilization; that is, it arises from the stabilization of Fe^{2+} in the octahedral site of the oxide as compared with the (pseudo)dodecahedral site of the perovskite (Burns, 1993; Yagi et al., 1979). The apparent crystal field stabilization has been used to estimate (or rationalize) partitioning between the two

phases. Malavergne et al. (1997) found that partitioning results are consistent with observations for inclusions thought to have originated in the lower mantle and proposed to be representative of a pyrolite composition (Kesson and FitzGerald, 1992). McCammon used Mössbauer measurements to show that a significant fraction of the iron in (Mg, Fe, Al)SiO₃ perovskite produced in multianvil experiments is Fe³⁺ (McCammon, 1997). The incorporation of Fe³⁺ is strongly coupled with the Al³⁺; this result does not, however, mean that the lower mantle is oxidized as pressure stabilized the Fe³⁺ ion (Frost et al., 2004; McCammon, 2005).

Both crystallographic and Mössbauer studies indicate that Fe²⁺ in silicate perovskite resides in the octahedral site (see Hemley and Cohen, 1992). Attempts have been made to determine the site occupancy of Fe²⁺ and Fe³⁺ from Mössbauer spectroscopy (McCammon, 1998). The spectra of (Mg_{0.95}Fe_{0.05})SiO₃ reportedly synthesized at low *f*_{O₂} indicate that the Fe³⁺ goes in the octahedral site, whereas higher *f*_{O₂} conditions result in Fe³⁺ on both sites. First-principles theoretical computations show that ferrous iron remains high spin in perovskite and is on the A-site (Caracas and Cohen, 2005a), but ferric iron undergoes a high-spin to low-spin transition in the pressure range of 100–125 GPa (Li et al., 2005).

A revolution in our understanding of the deepest mantle and high-pressure mineral physics was the discovery of the postperovskite phase in MgSiO₃ (Murakami et al., 2004a; Oganov and Ono, 2004; Tsuchiya et al., 2004), which appears to be stable for a wide range of compositions at pressures in the megabar range (Caracas and Cohen, 2005a,b). The application of the previously mentioned electronic and magnetic techniques to silicate postperovskite is challenging because of the need to carry out the experimental in situ at very high pressures (e.g., ~100 GPa and above), and much input on the properties of postperovskite has come from theoretical computations. Nevertheless, a number of measurements are being carried out, including NRIXS and XES, which are providing acoustic velocities and identification of the iron as low spin (Figure 21). A growing number of experimental studies are being performed in spite of the challenges (Mao et al., 2006b). Experiments show that most iron in Al-bearing postperovskite is ferric iron (Sinmyo et al., 2006), consistent with first-principles theory (Li et al., 2005). First-principles DFT calculations show

ferrous iron to be unstable to disproportionation to ferric iron (in postperovskite) and metallic iron in an hcp-Fe phase (Zhang and Oganov, 2006), consistent with experiment (McCammon, 2005). Theory predicts ferrous iron to be high spin to pressures well above the highest pressures in the mantle in both perovskite and postperovskite (Caracas and Cohen, 2005a; Stackhouse et al., 2006).

2.13.5.4 Volatiles

Volatile uptake and recycling in high-pressure phases provide important constraints on the Earth's history (Bercovici and Karato, 2003; Brooker et al., 2003; Kerrick and Connolly, 2001; Sanloup et al., 2002b,c). Under pressure, volatiles can become structurally bound components, either as stoichiometric compounds or as soluble components in nominally anhydrous phases (Williams and Hemley, 2001). Dense hydrous silicates present different degrees of hydrogen bonding under ambient conditions. The prototype system is H₂O, which is discussed further later in the text.

Pressure-induced disordering of crystals may be intimately associated with the behavior of the hydrogen through sublattice amorphization or melting (e.g., Duffy et al., 1995b; Nguyen et al., 1997; Parise et al., 1998). The pressure dependence of OH stretching modes shows a tendency toward increased hydrogen bonding, but decreased hydrogen bonding is also observed (Faust and Williams, 1996; Hemley et al., 1998a). These results, together with the evidence for disordering, point toward the importance of hydrogen–hydrogen repulsions. Finally, an example of the change in bonding affinities is the formation of iron hydride at high pressure. It produces a dhcp structure at 3.5 GPa, which is stable to at least 60 GPa (Badding et al., 1992).

There is growing evidence for pressure-induced chemical interactions in rare gases. The low abundance of xenon in the atmosphere (relative to cosmochemical abundances) is a long-standing problem in geochemistry and has given rise to the proposal that the element may be sequestered at depth within the Earth. Near-IR spectroscopy and electrical conductivity measurements show that solid Xe becomes metallic at 130–150 GPa (Eremets et al., 2000; Goettel et al., 1989; Reichlin et al., 1989). Prior to metallization, the material

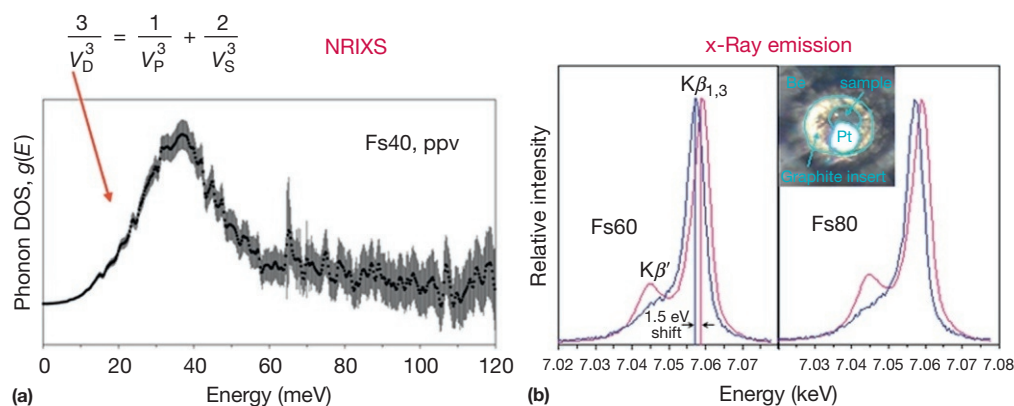


Figure 21 (a) NRIXS spectra showing the phonon DOS for postperovskite phase of Fs40 at 130 GPa after temperature quench from 2000 K. Reproduced from Mao WL, Mao HK, Sturhahn W, et al. (2006) *Science* 312: 564–565. (b) x-Ray emission spectroscopy (XES) of the material measured in situ at high pressure. Reproduced from Mao WL, Mao HK, Sturhahn W, et al. (2006) *Science* 312: 564–565.

transforms from the fcc to the hcp structure (Jephcoat et al., 1987). Recent studies have shown that the equilibrium transition pressure is as low as 21 GPa (Caldwell et al., 1997). Experiments to 30 GPa and theoretical calculations to inner core pressures reported in this study show (surprisingly) no evidence for chemical affinity for Xe and Fe (Caldwell et al., 1997). The melting points of Xe and Ar increase initially with pressure (Jephcoat, 1998) but then flatten out; this has been interpreted as arising from s–p–d hybridization (Ross et al., 2005).

We also briefly mention planetary gases and ices at high pressure. Dense hydrogen is the most abundant element in the solar system. Accurate determinations of its electronic and magnetic properties to multimegabar pressures (>300 GPa) over a wide temperature range and ultimately to the high-density plasma are crucial for planetary geophysics. Both optical spectra and direct measurements of the electrical conductivity show that solid hydrogen remains insulating to at least 230 GPa at low temperatures (<200 K) (Hemley et al., 2002). On the other hand, the dense hot fluid exhibits metallic conductivity 140–200 GPa (Collins et al., 2001; Nellis et al., 1996). Recent developments have made it possible to contain hydrogen at 1000 K at static megabar pressures, allowing measurements to be performed on the dense hot fluid over this P – T range (Gregoryanz et al., 2003).

The changes in bonding and electronic structure of various ices are particularly important for planetary science. The symmetrical hydrogen bond state of ice at 60 GPa reveals intriguing quantum mechanical tunneling effects associated with the transition (Goncharov et al., 1996). There is a steep increase in melting temperature of the ionic symmetrical ice phase (Goncharov et al., 2005a; Lin et al., 2005a). Sublattice melting has also been explored (Cavazzoni et al., 1999; Kato et al., 2002). There are predictions to other high-pressure forms above 0.3 TPa (Benoit et al., 1996; Cavazzoni et al., 1999). Most recently, it has been found that the combination of x-ray irradiation and high pressure can break down H_2O to form an alloy H_2 and O_2 at pressures up to at least ~50 GPa and stable relative to H_2O to ~500 K (Mao et al., 2006a).

2.13.5.5 Iron and Iron Alloys

The Earth's core plays a central role in the evolution and dynamic processes within the planet. As the major constituents of the core, iron and its alloys hold the key to understanding the nature of this most enigmatic region of the planet (Hemley and Mao, 2001). Geophysical observations have uncovered surprising inner core properties, such as seismic anisotropy, super rotation, and magnetism (Glatzmaier and Roberts, 1996; Niu and Wen, 2001; Romanowicz et al., 1996; Song and Helmberger, 1998; Song and Richards, 1996; Su et al., 1996; Tromp, 2001). These observations are supplemented by geodynamic simulations (Buffett, 2000, 2003; Buffett and Wenk, 2001; Karato, 1999; Olson and Aurnou, 1999). Ab initio theoretical calculations have been applied to examine and predict melting, phase stabilities, elastic anisotropy, and magnetism of iron beyond experimental capabilities (Alfé et al., 1999, 2000; Belonoshko et al., 2003; Laio et al., 2000; Steinle-Neumann et al., 2001; Stixrude and Cohen, 1995; Vocadlo et al., 2003). Theory shows that the bcc phase is stabilized by magnetism. There had been much discussion of bcc as the possible structure for iron in the Earth's

inner core, but calculations showed that bcc iron is mechanically unstable at high pressures due to the loss of magnetism with pressure (Stixrude and Cohen, 1995). On the other hand, the hexagonal phase (ϵ -Fe) is nonmagnetic. The reflectivity of iron decreases markedly across the bcc–hcp transition; measurements to 300 GPa showed that this low reflectivity continues to much higher pressure (Reichlin et al., unpublished).

Pressure effects on the valence band densities of states and magnetic properties of Fe are being measured with the new synchrotron x-ray techniques described in the preceding text. Large differences in DOS are predicted between bcc Fe and the two closed-packed phases (hcp and fcc). Spin-dependent K_β emission fine structure can be used to probe localized magnetic properties with XMCD. The element-specific nature of XES and XMCD will be particularly important in the study of transition metal and rare earth alloys. High P –TXAS and XRD are providing electronic and structure information for iron melt and crystals (Jackson et al., 1993; Sanloup et al., 2002a). High P – T NRFS is providing information on Mössbauer effect and magnetism (Jackson et al., to be published), and high P – T NRIXS coupled with hydrostatic equation of state data yields phonon densities of state, bulk longitudinal and shear wave velocities, heat capacity, entropy, Debye temperature, and Grüneisen parameter (Lübbert et al., 2000; Mao et al., 2001; Struzhkin et al., 2001).

2.13.6 Conclusions

A range of high-pressure techniques are now available to investigate changes in bonding electronic and magnetic structures induced by pressure in the Earth and planetary materials. In general, recent work has shown that a variety of techniques are required to understand the evolution of these complex systems under pressure. This includes the use of newly developed theoretical methods, which are providing increasingly accurate predictions for energetic properties of these materials under extreme conditions. There is much to be learned about the origin of the behavior of transition metal compounds and solid solutions at high pressures. The study of transitions in Mott insulators is a particularly important current problem, with implications for condensed-matter theory as well. Future work should also focus on both defect properties and polyphase aggregates at high P – T conditions: Rocks are composite material, yet most mineral physics studies assume that the electronic and magnetic properties of the rock can be determined by adding up the contributions from the component mineral phases. An important question is the extent to which the electronic properties of the composite need to be considered (i.e., from interfacial, nanophase properties (Maxwell-Garnet, 1904)). The effects of such large changes in pressure on chemical properties are established. In general, the large perturbation of pressure on the electronic structure of materials suggests that the partitioning among different phases may be difficult to predict from ambient pressure measurements.

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2.14 Methods for the Study of High P–T Deformation and Rheology

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2.14.1 Introduction

This section is devoted to recent studies that aim to define the rheological properties of Earth materials at high pressure and high temperature. The frontier has been defined by the bringing together of exciting new tools for studying these properties. Multi-anvil high-pressure apparatus, which are capable of reaching into the lower mantle with hydrostatic pressure, are being altered to provide a deformation environment. Samples recovered from these systems deliver information about the deformation process. Synchrotron x-rays have opened new vistas with their ability to see into the pressure chamber and yield stress and strain of the sample *in situ*. Around these metrics, new tools are being developed that can control the sample environment. The next phase of these studies will probably see us creating conditions of the deep lower mantle with well-characterized sample environments and precise measures of the quantitative flow process. Along the way, we will gain insights into aggregates and how stress is distributed among the grains. Information on texture, elastic anisotropy, and stress as a function of pressure, temperature, and environment will be derivable from this information.

The dynamic nature of Earth, including phenomena ranging from earthquakes and volcanic eruptions to plate tectonics and mantle convection, is responding to the plastic nature of the materials of Earth's mantle. An improved understanding of these dynamic features of Earth will follow from insights into the flow properties of the rocks that make up Earth. This fundamental principle has defined a field within the Earth sciences that we call 'rheological studies.'

Rheological studies are among the most challenging of the experimental fields that strive to provide information about

Earth. Plastic properties are not state variables; that is, these properties do not depend solely on the classical thermodynamic state of the material. In addition to pressure, temperature, and chemical potentials, the plastic properties depend on the history of the sample. History produces the sample with a dislocation density, a grain size, and a texture. History adds the dimension of time. On Earth, time scales span millions, if not billions, of years, with strain rates slower than 10^{-15} s^{-1} , while in the lab, experiments that last for a week are considered long and strain rates slower than 10^{-7} s^{-1} are considered imperceptibly slow. If we wish to work in the laboratory at geological strain rates, then a 1-m-long sample will change its length by 30 μm in 100 years.

Plastic flow belongs to the realm of irreversible thermodynamics, where the concept of steady state replaces that of equilibrium in reversible thermodynamics. Steady state is then governed by an extreme in the rate of entropy production rather than an extreme in the entropy. So too, in rheological studies, steady state becomes a goal of experimental probing. Steady state on a macroscopic scale is indicated by the time independence of both stress and strain rate. On a microscopic scale, the defect structure and the grain size must become time-independent. Here at least, the role of history is minimized in that history is no longer altering the properties of the sample, and it is hoped that the history prior to the experiment has been removed by the lab-induced flow process. Yet, while steady state is a necessary condition for a well-defined experiment, it is not a sufficient condition. For example, a difference in grain size between two samples can lead to very different flow characteristics. Furthermore, the confirmation of steady state is virtually impossible to achieve. In this manner, again,

steady state is quite similar to the state of equilibrium, which is also difficult to verify.

Indeed, natural processes are not restricted to steady-state flow. Phenomena including earthquakes, formation of ductile shear zones, and even glacial rebound occur outside of the steady-state regime. To provide the necessary information to describe these nonsteady-state processes, an even more complex description is required.

Another complicating feature of rheological processes is their dependence on small amounts of some atomic species. The flow process generally involves movement of atoms. This movement is often greatly influenced by point defects in the solid, indeed, by participants that may have a very small concentration in the material. In geological systems, water has extreme effects on the rheological properties of some minerals (quartz and olivine are good examples). Thus, a well-characterized rheological experiment will demonstrate a steady state and will characterize the sample and sample environment in terms of grain size, texture, dislocation type, and density, in addition to defining the chemical potentials of all active species.

With all these support characterizations in place, the quantitative flow law is defined as the relation between the stress, σ , and strain rate, $\dot{\epsilon}$, where stress is a measure of the deviatoric stress, often a differential stress, and the strain rate indicates the rate of deformation. A typical high-temperature semiempirical steady-state relation between stress and strain rate is given by

$$\dot{\epsilon} = A(\sigma/\mu)^n (b/d)^m \exp - \left(\frac{E^* + PV^*}{RT} \right) \quad [1]$$

where b and μ are the Burger's vector for the active dislocation and the shear modulus of the material, both intrinsic properties of the material. d is the grain size, R is the rare gas constant, P is the pressure, and T is the temperature. The other parameters A , n , m , E^* , and V^* are flow parameters that are specific to the particular flow mechanism and generally need to be determined empirically. The variables are arranged so that the values within parentheses are dimensionless. Flow by diffusion is generally associated with $n=1$ and m in the range of 2–5, while dislocation-controlled flow obtains with $m=0$ (no grain size dependence) and n in the range of 2–5. In order to define all the parameters in this relation, the experimental protocol needs to be defined to measure strain rate as a function of stress (to define n), grain size (to define m), temperature (to define E^*), and pressure (to define V^*). These measurements should be made on a sample that has achieved steady-state flow (unless one wishes to characterize transient creep) in a well-defined environment.

2.14.2 Importance of High-Pressure Rheology Measurements

Laboratory data do not give us a simple estimate of viscosity of Earth. First of all, viscosity, the ratio of the stress to strain rate, depends on the level of stress, as seen in eqn [1]. Thus, to estimate viscosity, we must know the amount of stress. Second, extrapolation over several orders of magnitude of strain rate can lead to large errors. The rheological properties of Earth's

mantle can be inferred from analyses of geodynamic data such as postglacial crustal movement and gravity anomalies (Mitrovica and Forte, 1997; Peltier, 1998). The measurements are enabled by both a large length scale and a long time scale. However, even these data are insufficient to define Earth rheology. The depth resolution of postglacial rebound data is limited to ~ 1000 km (Mitrovica and Peltier, 1991). Furthermore, the amount of strain required for postglacial rebound is much smaller than the strain encountered in convection. In so much as the rheology maintains a memory of previous deformation, small strain rheology may be different from large strain rheology (Karato, 1998). Gravity data (e.g., the geoid) have a better sensitivity to radial variation in viscosity in the deep mantle (Hager, 1984), but they suffer from non-uniqueness (King, 1995; Thoraval and Richards, 1997). Laboratory studies of rheology can provide information about mechanism, stress and strain dependence, and other variables such as chemical or phase dependence. Therefore, experimental studies on mineral rheology remain a vital component in inferring mantle rheology.

2.14.2.1 Lateral Variation of Asthenosphere Viscosity

As an example, here we illustrate how the activation volume helps constrain the lateral variations in asthenosphere viscosity. We define the asthenosphere viscosity as the lowest viscosity in the upper mantle in a specific region. Generally, the temperature profile is the dominant variable to define regional viscosity. We approximate the mantle temperature profile as adiabatic with a thermal boundary layer at the top. The details of the thermal boundary layer depend on the age of the crust in the region. Older regions have a deeper cooling. Figure 1 illustrates three temperature profiles that could be representative of 20-My-old oceans, 80-My-old oceans, and very old continental cratons. The geotherm reaches the adiabat at different depths in these models owing to the time that

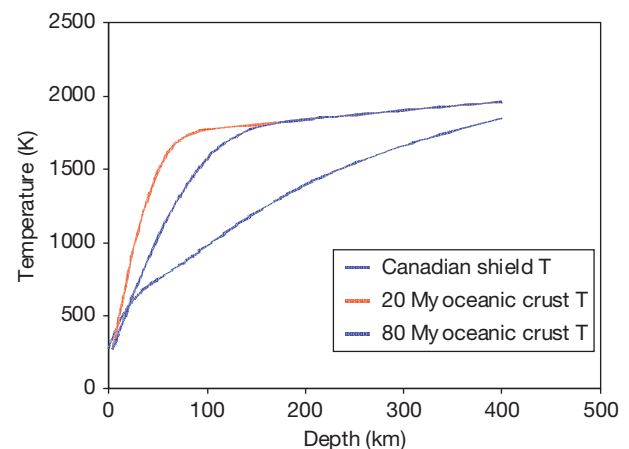


Figure 1 Radial temperature profiles for different geologic settings. Ocean profiles are calculated assuming a cooling lid on a mantle adiabatic temperature gradient. The Canadian shield is calculated assuming a conduction gradient with localization of radiogenic elements in the crust. Reproduced from Li L (2003) *Rheology of Olivine at High Temperature and High Pressure*, 137 p. SUNY at Stony Brook, Stony Brook, NY.

conductive cooling is operating from the surface. The lowest viscosity will not occur at least until the depth that the temperature is on the adiabat. Because pressure increases with depth, the variation in magnitude of the lowest viscosity from region to region will depend on the activation volume of the flow process. Estimates of olivine's activation volume for power-law creep range from 0 to 30 cc mol^{-1} . Figure 2 illustrates the depth dependence of viscosity as a function of activation volume for a fixed stress along these model geotherms. An activation volume of 20 cc mol^{-1} would render the minimum viscosity under the Canadian shields 6 to 7 orders of magnitude greater than the minimum viscosity under 20-My-old oceans for the same shear stress, while a 0 activation volume would have no difference in minimum viscosity.

These conclusions are based on maintaining the same dominant slip system as pressure is increased. Karato and Wu (1993) argue that this large-pressure-dependent process will force a change in the deformation mechanism to diffusion by the middle of the upper mantle. While diffusion flow is much slower than dislocation flow at atmospheric pressure, the presumed low activation volume for diffusion suggests that pressure will not significantly slow down diffusion flow. Nonetheless, we see the manner that laboratory studies enters the Earth dynamic issues.

The main experimental challenge is to measure the stress and strain rate at mantle pressure and temperature conditions of a specimen that has reached steady-state flow. Low-pressure tools have been used to precisely apply a force or a strain rate to define the flow of olivine (Chopra, 1997; Durham and Goetze, 1977; Green and Borch, 1987; Hirth and Kohlstedt, 1995; Karato et al., 1986; Kohlstedt et al., 1984; Mei and Kohlstedt, 2000; Paterson, 1990), albeit at pressure lower than 0.3 GPa (compared to 13 GPa at the olivine stability limit). Torsion apparatus has been applied to study the high shear strain deformation with pressure up to 0.3 GPa (Bystricky et al., 2000).

The force–displacement tools have been pushed to a higher pressure using the Griggs-type solid medium apparatus (up to 2.5 GPa) (Green and Borch, 1987; Karato and Jung, 2003; Ross et al., 1979). Molten salt cell assemblies help maintain a quantitative measure of the stress at pressures up to 2.2 GPa (Borch and Green, 1989; Green and Borch, 1989). Development of the large volume multi-anvil press (e.g., Bussod et al., 1993) allowed the synthesis of deformed samples at upper-mantle pressure for microstructure examination (Ando et al., 1997; Cordier et al., 2002; Karato, 1989; Karato et al., 1993; Rubie et al., 1993). Results from these higher pressure experiments have generally been accepted as qualitative.

2.14.2.2 Earthquakes

A second example of the importance of laboratory data concerns the origin of deep-focus earthquakes. The standard friction-mitigated processes should not be operative at depths greater than about 20 km, yet earthquakes persist to depths of 700 km. The process that is responsible for the space–time localization of the stress drop is still unclear. Several alternative mechanisms for the stress release instability have been suggested over the years, including a thermally induced plastic instability (Hobbs and Ord, 1988; Ogawa, 1987), instabilities accompanying recrystallization (Post, 1977), dehydration embrittlement (Jiao et al., 2000), and instabilities associated with polymorphic phase transformations (Green and Borch, 1989; Kirby et al., 1991); see also reviews by Green and Houston (1995) and Kirby et al. (1996). Again, the main reason for the uncertainty that still exists is the poor knowledge of material properties at high pressures. The rheological properties of deep Earth materials have been missing so far (Hobbs and Ord, 1988; Karato et al., 2001), thus impeding modeling of the processes. Similarly, a greater understanding of the

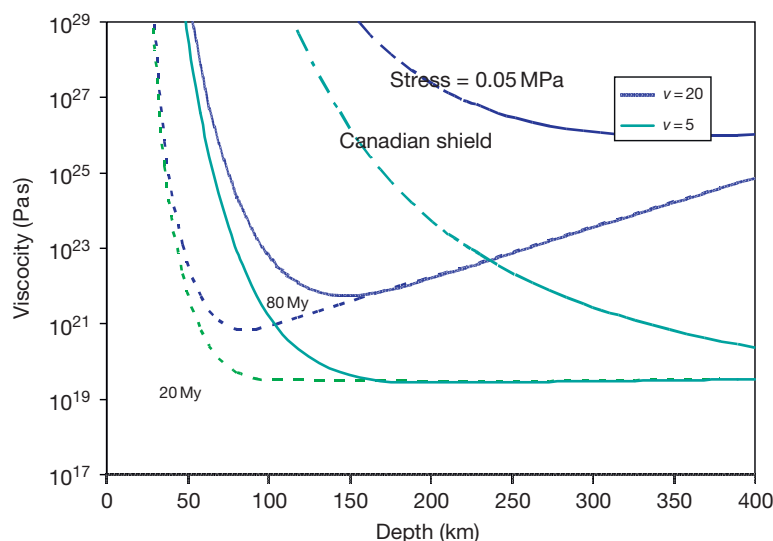


Figure 2 Viscosity versus depth for different geotherms and different activation volumes. The temperatures were calculated from standard cooling profiles for the different regions. Reproduced from Li L, Raterron P, Weidner D, and Chen J (2003) Olivine flow mechanisms at 8 GPa. *Physics of the Earth and Planetary Interiors* 138: 113–129.

possible shearing instabilities and kinetics associated with the phase transformations of olivine to wadsleyite and ringwoodite (Burnley et al., 1991; Green et al., 1990) and of the possibility of faulting associated with dehydration of the dense hydrous magnesium silicates (Jung and Green, 2004) needs well-controlled deformation experiments under deep mantle conditions.

2.14.3 High-Pressure Tools

2.14.3.1 Stress Measurement

Measurement of deviatoric stress is key to quantifying the rheological properties of a material. Stress provides information about strength relative to the laboratory time scale. Stress, measured in conjunction with ductile strain, can yield flow laws within the context of the state of the sample. The crucial ingredient to facilitate such studies is the development of a stress meter.

Experiments operating below 5 GPa apply the deforming force directly to the sample and design various strategies to measure the magnitude of this deforming force. Stress is the ratio of force to sample area. Typically, a load cell placed in series with the deforming piston defines this force along the deforming column. For systems operating above 1 GPa confining pressure, combinations of friction between the force gauge and the sample and forces that support the piston, such as in the multi-anvil system, continually degrade the ability to relate a measured force to the sample stress. These problems become progressively more acute as the pressure of the sample becomes higher.

A revolutionary technique for stress and strain measurements under high-pressure (and temperature) conditions *in situ* has now become feasible with the use of high-energy x-rays generated by a synchrotron radiation facility. These new tools are now being explored and their limitations defined. The exceptional quality of these tools rests on the fact that they directly monitor the sample. Stresses are measured in the sample. Different positions in the sample can be isolated to test for stress uniformity. Measurements of stress and strain can be time-resolved with a precision of about 1 min. Strain is also obtained from images of the sample. Distribution of strain with position and time can be defined; all this is done with a current accuracy about 10 MPa in differential stress and 10^{-4} in strain (Weidner et al., 2010).

A uniaxial stress will introduce elastic strains in the sample. The strain parallel to the axis of compression will generally be larger than the strain perpendicular. The material's elastic moduli, through Hooke's law, quantitatively define the relationship between these strains and the imposed stresses. X-rays sample the distance between lattice planes (called d-spacing) whose normals are parallel to the diffraction vector, which is the bisector between the incident x-ray and the detector. The lattice spacings reflect elastic strain and are insensitive to plastic strain. Figure 3 illustrates a Debye ring that would be observed from a powder sample in a stress field using a monochromatic x-ray beam and an area detector. The lattice spacing is related to the distance from the center of the image to the Debye ring through Bragg's law. For the angle Ψ of zero, the lattice spacing reflects that measured parallel to the x_1 direction. For Ψ of 90° , the x-rays are sampling grains aligned parallel to the x_2 direction.

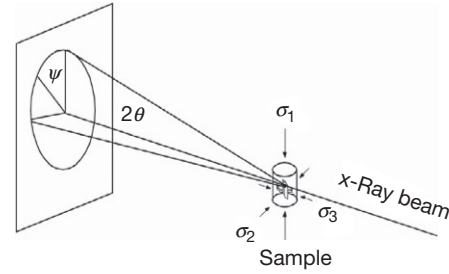


Figure 3 x-Ray diffraction geometry. The stress field of the sample is illustrated by σ . In the DDIA configuration $\sigma_2 = \sigma_3$.

The strains deduced from these measurements compared with ambient conditions are related to the stresses by

$$\varepsilon_{ij} = \sum_{k=1}^3 \sum_{l=1}^3 s_{ijkl} \sigma_{kl} \quad [2]$$

where s is the elastic compliance tensor.

A strategy for measuring stress comes from mapping out the d spacing as a function of Ψ . The values of the elastic moduli are still required, but the details of anisotropy are less critical to yielding of precise measurements. With a precision of 10^{-4} for the lattice spacing and a typical elastic modulus of 200 GPa, it should be possible to resolve differential stresses of ~ 20 MPa. Singh has reduced the elasticity equations to a closed form solution for several crystal-symmetries and gives a concise summary in Singh et al. (1998).

In the actual case, more than one set of diffraction planes will produce Debye rings similar to the one illustrated here. Each will be circular in shape for a hydrostatic stress, but distorted by nonhydrostatic stress. The amount of distortion may be different if the elastic compliance tensor is not isotropic. To evaluate this in detail, we need to be careful to account for the crystal orientation when defining the compliance tensor. Thus, in a nonhydrostatic stress field, crystallographic planes with different orientations change their spacing by different amounts. For cubic crystals, the relationship between the Ψ dependence of strain and the differential stress, $\Delta\sigma$, is given by (Singh, 1993)

$$\varepsilon_{hkl}(\Psi) = \Delta\sigma/3 \{1 - 3\cos^2(\Psi)\} \{ (S_{11} - S_{12})(1 - \Gamma(hkl)) + S_{44}\Gamma(hkl)/2 \} \quad [3]$$

Each diffraction peak corresponds to a set of lattice planes defined by the Miller index, hkl . In an anisotropic crystal, the elastic moduli will depend on the particular set of planes that are considered. The function, $\Gamma(hkl)$, varies from 0 to 1, and reflects the elastic moduli for the orientation of the particular diffraction peak. Thus, for a particular diffraction plane, hkl , the right-hand bracket contains a constant value. Then, ε_{hkl} varies in a fixed manner with the angle, Ψ . ε_{hkl} is the deviatoric strain and is defined as the strain relative to the hydrostatic state. Measuring the lattice spacing for a particular hkl at $\Psi = 0^\circ$ and 90° is enough to define the differential stress. This relation for cubic symmetry is generalized by Singh et al. (1998) for all crystal symmetries. In the case where the stress field is not uniaxial, but more complicated, this analysis yields the stress field in the plane perpendicular to the x-ray beam, but does not recover the entire stress tensor.

This methodology was first applied in a diamond anvil cell by Kinsland and Bassett (1977) by passing the x-ray beam through a Be gasket, perpendicular to the axis of the diamonds. The multi-anvil system has not been accessible by this technique because the anvils themselves cast a shadow and limit the range of Ψ where the diffracted signal can be observed. However, both cubic BN and sintered diamond anvils are hard as well as x-ray transparent. Thus, it is now possible, using these anvils, to observe diffraction spectra in any plane relative to the incident beam in a multi-anvil device.

This tool can be used with monochromatic x-rays for angle-dispersive measurements and with white x-rays for energy-dispersive methods, both with specific advantages and disadvantages. With white x-rays, spectra need to be collected for different values of Ψ through collimators that fix the 2θ value. A conical slit system (Li et al., 2004a,b) can be used for this purpose, as illustrated in Figure 4. The slit itself is created by two concentric cones, whose angle is the desired diffraction angle for white, energy-dispersive diffraction. Solid-state detectors (SSDs) with energy discrimination are placed at specific values of Ψ behind the slit system. Each detector is calibrated independently. Lattice spacings are used, as illustrated earlier, to define the differential stress. The advantage of this system is that the diffracted signal is collimated, allowing diffraction from the sample to be isolated from that of the pressure medium. Monochromatic x-rays are more versatile in defining the orientation of the deformation ellipse and are quite useful when the orientation of the stress field is not well defined by the experimental geometry.

Each diffraction peak represents a different subpopulation of grains within the sample. Generally, grains that are oriented so as to contribute to one diffraction line are not oriented to contribute to another. If all the diffraction lines define the same values of stress, then the stress field is fairly homogeneous within the sample, with no distinctions on the basis of the orientation of the crystallites. However, it is quite common for the different peaks to provide different values of the differential stress. This indicates that these different subpopulations

of grains experience different stresses. The average stress in the sample, that is the average of force per unit area, will simply be some average of the subpopulation stresses. Later, we will discuss the origin of this stress heterogeneity.

2.14.3.2 Strain Rate Measurement

Synchrotron x-rays can also be used to measure sample length. Direct images of the sample can be obtained using an incident beam whose dimensions are larger than the sample. Platinum or gold foils above and below the sample are easily viewed. The x-ray image is obtained by projecting the x-ray onto a fluorescent screen that is viewed with a CCD camera through a magnifying system. A typical image is shown in Figure 5. The horizontal lines in this image are gold disks placed at the ends of the sample. The black edges are the shadows of the opaque tungsten carbide anvils. Cubic boron nitride anvils are transparent and can be used to view the entire sample as they do not cast such a shadow. Figure 4 illustrates the position of the microscope for these measurements. The fluorescent screen is located on-axis inside the conical slit system. We determine that, by comparing two images, strains of 10^{-4} can be measured. For images taken 100 s apart, this allows resolution of strain rates of 10^{-6} s^{-1} .

With these tools of stress and strain rate, quantitative flow laws defined by relations such as eqn [1] can be defined. Inspired by the new insights into the high-pressure apparatus, improvements were made in the high-pressure instrumentation that could provide a steady-state flow for relatively large strains in samples at high pressure and high temperature.

2.14.3.3 New High-Pressure Deformation Devices

The use of x-rays to measure both stress and strain directly in the sample, without a proxy such as a force gauge, frees the conceptual design of the deformation equipment. When using a force gauge, one must measure both the force and displacement of a piston and this piston must only push on the sample.

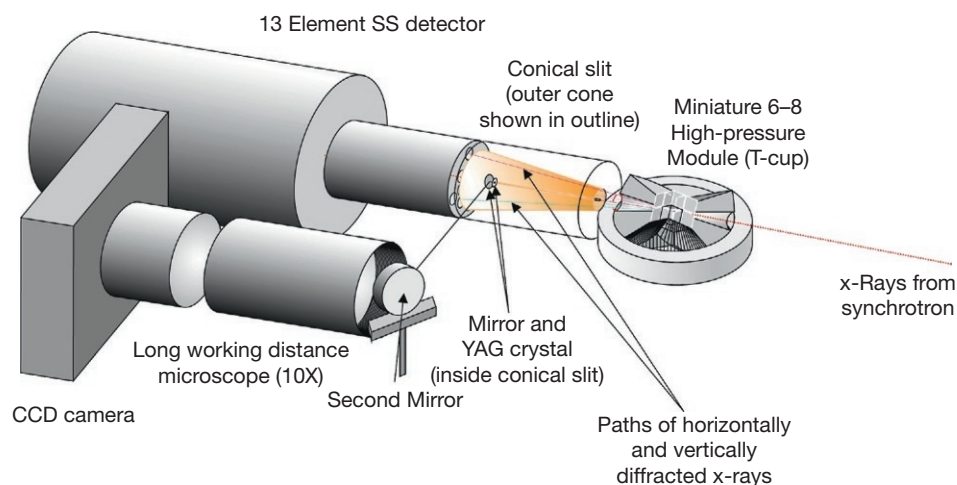


Figure 4 The conical slit shown with the T-cup device and a multielement energy-dispersive detector. The diffracted x-ray from the sample is collimated by a conical slit system, which allows diffraction at a fixed 2θ angle. The multiple-detector is placed behind the slit system to capture the diffracted beam for several values of Ψ .

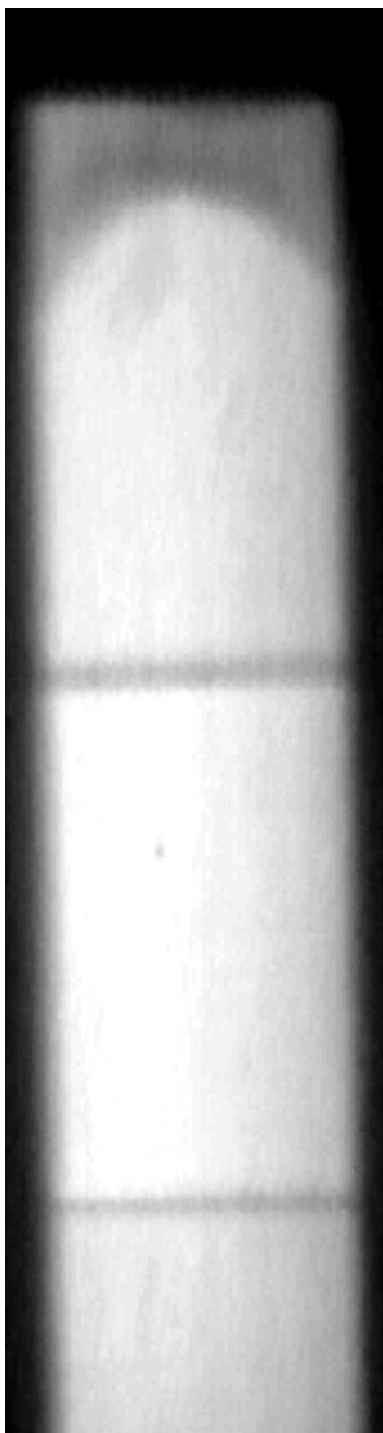


Figure 5 Shadowgraph image of a sample at high pressure and temperature. The black boundary is defined by tungsten carbide anvils; the dark lines are from metal foils within the sample.

Friction on the piston, deformation of the piston, elastic and thermal responses of the piston, all must be quantified in order to define the force–displacement of the sample. The piston must push on the sample and only on the sample. With the stress and strain of the sample measured directly, these issues are no longer important. The entire anvil can serve as the deforming unit. Indeed, two new systems have emerged that

take advantage of the large volume high-pressure apparatus and use the loading anvils as the instrument to create a deviatoric stress.

The first of these devices is called the deformation DIA (DDIA; [Durham et al., 2002](#); [Wang et al., 2003](#)). This system is derived from the DIA apparatus, which has been extensively used on synchrotron x-ray sources ([Shimomura et al., 1985](#)). This apparatus forces six anvils to synchronously advance on a cubic pressure medium ([Figure 6](#)). The DDIA modification is to add hydraulic jacks to push on the upper and lower anvils. This allows the application of a nonhydrostatic stress to the entire cubic cell assembly, while at the same time, the main ram can be adjusted so as to maintain a constant pressure. A typical assembly is illustrated in [Figure 7](#). The cylindrical geometry of the sample assembly includes hard pistons above and below the sample chamber that transmit the stress produced by the loading anvil to the sample. The independent upper and lower anvils can be driven to produce a constant strain rate in the sample for very large values of strain (in excess of 50%) as the side anvils are withdrawn to maintain a constant volume. The side anvils need to be x-ray transparent in order to measure x-ray diffraction in the horizontal plane. Cubic boron nitride and sintered diamond have both been used for this purpose. The final system allows most samples to achieve a steady-state condition in which the stress and strain rate can be measured *in situ*.

The second system that has been recently developed is called the rotational Drickamer cell ([Yamazaki and Karato, 2001](#)). This system is patterned after the Drickamer cell ([Perez-Albuerné et al., 1964](#)) that has been used on synchrotron sources. This cell is pressurized by two opposed anvils with a containment ring ([Figure 8](#)). The deformation is obtained by rotating one of the two opposed anvils. This rotation must be done while the anvils are being forced into the sample. A series of hard pistons and furnace elements transmit the rotation from the anvil into the sample ([Figure 8](#)). The rotation produces a shear strain and stress that varies from the center to the outer edge of the disk-shaped sample. Strain markers that can be imaged with the synchrotron x-ray source, used in conjunction with diffraction-derived stress, define the pertinent variables for these experiments. The most significant effect of rotational strain systems is their ability to induce very large amounts of strain in the sample. Strains of a few hundred per cent are possible. These systems are well suited for evaluating texture development during deformation at high strain levels.

2.14.3.4 Forced Oscillation at High Pressure and High Temperature

In the last few years, the use of the DDIA has expanded beyond deformation experiments. Instead of driving the top and bottom anvil toward each other at constant rates in conventional deformation experiments, the deformation anvils can be driven in an oscillating fashion ([Li and Weidner, 2010](#)). The surrounding anvils can also be controlled simultaneously to maintain a constant pressure. Similar to a constant strain rate deformation experiment, forced oscillation experiments use synchrotron x-ray as a probing tool. The sample is stacked with a stress-proxy in a high-pressure cell assembly. A CCD camera captures the images of the sample and the proxy during

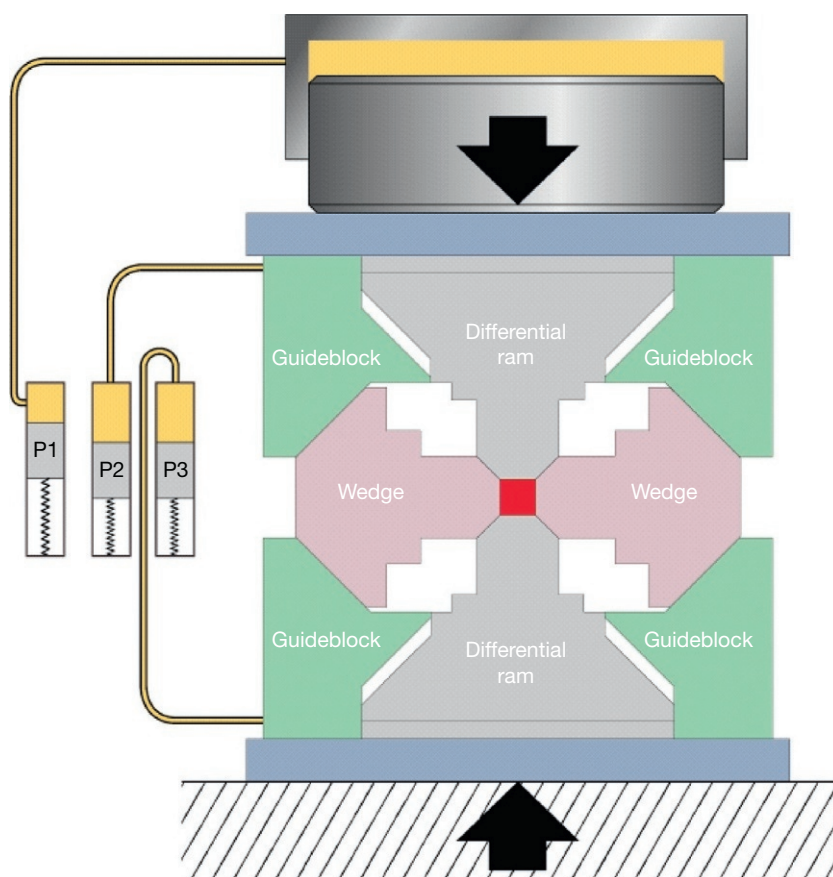


Figure 6 Illustration of DDIA. Four of the six anvils are illustrated (the front and back are not illustrated). P1 is a hydraulic pump that pushes the main jack in the directions of the arrows. This jack drives all six anvils into the sample. Pumps P2 and P3 drive the upper and lower anvils into (out of) the sample independently of the main jack. Figure created by Sabrina Fletcher of LLNL.

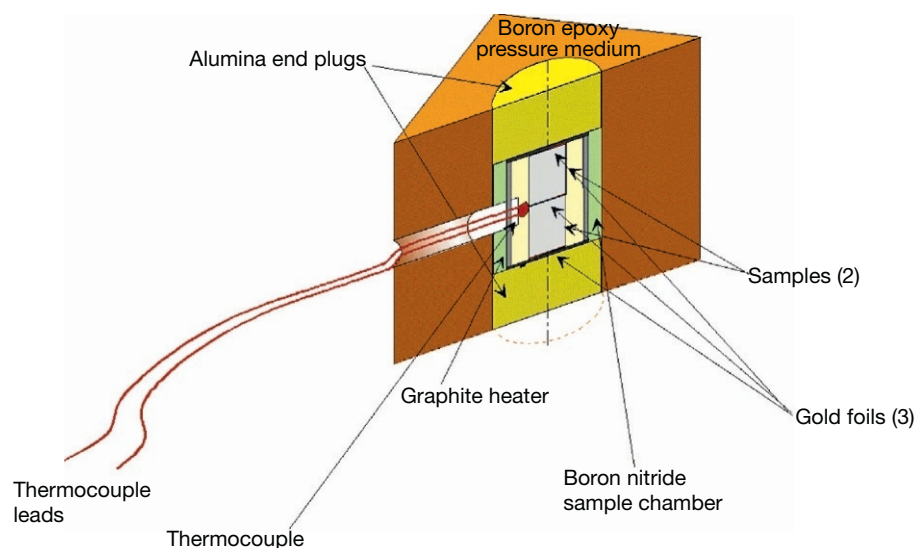


Figure 7 Typical cell assembly. The alumina end plugs serve as deformation anvils at high pressure and temperature.

the oscillation cycle. The strain of the proxy and sample is measured, with the resulting amplitude ratio indicating the ratio of the elastic moduli and the phase lag indicating the attenuation. This protocol introduces a new variable into the mechanical testing, that is, the frequency. The range

of frequency DDIA can accommodate as defined by the hydraulic system is Hz and below. This method can be applied at the pressure and temperature range obtainable in DDIA. It requires software control but minimal modification of DDIA apparatus and detectors.

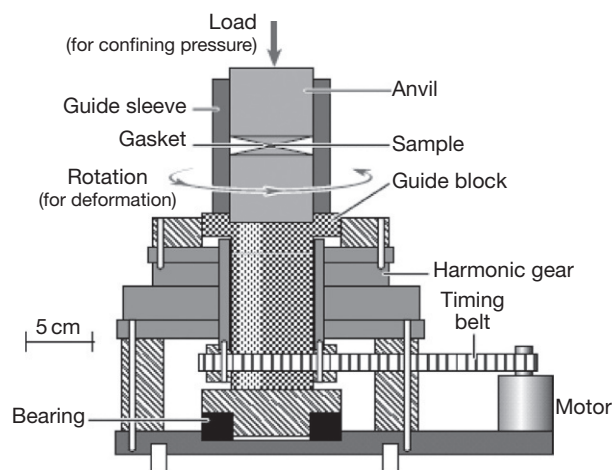


Figure 8 Rotational Drickamer apparatus. The load is applied vertically and the top and bottom anvils rotate relative to each other by virtue of the motor and the bearing assembly. The sample is sandwiched between two opposing anvils. Figure reused from Yamazaki D (2001) *Review of Scientific Instruments* 72: 4207, with permission. Copyright 2001, American Institute of Physics.

2.14.3.5 Synchronized Stress and Strain Measurement

In high-pressure dynamic loading experiments, stresses are often inferred from a stress proxy such as alumina even though stress can be measured from the sample from x-ray diffraction directly. However, in this case, the strain and stress of the sample cannot be measured simultaneously. The proxy stress can be measured simultaneously with the strain since they are both determined from the length changes of the sample and proxy, which are recorded in x-ray images. The x-ray image is taken by a CCD camera at millisecond shutter speed and requires an x-ray beam size of about 2×2 mm. Stress that is determined by an x-ray diffraction spectrum using multi-element SSD requires an acquisition time close to 500 s and a beam size of 50×50 μm . To synchronize the proxy and sample strain measurement, while gathering a diffraction signal as well, an x-ray beam shutter device has been designed. The shutter is triggered to switch from 50×50 μm slits mode to open every 30° following the sinusoidal curve (Li and Weidner, 2010). With deformation device, shutter, CCD camera, and SSD all synchronized, a complete stress–strain data set can be recorded 12 times per cycle. Even though each data point is recorded at a different time, a sinusoidal stress and strain curve can be reconstructed to derive phase-lag information. The synchronization of stress and strain not only allows differentiation between total strain and elastic strain, but also yields rich information about the activity of the slip systems in the material. This method is limited to the frequency at the mHz level because of the long collection time of x-ray diffraction patterns.

2.14.3.6 The Instruments of Flow

Laboratory determinations of flow laws obtain relevance to flow in the Earth by connecting the microscopic process that enables flow in both arenas. Several types of mechanisms that allow plastic flow are operating when a solid is experiencing a

deviatoric stress. However, the most successful mechanism will dominate the flow. As categorized in Ashby (1972) and presented for many materials in Frost and Ashby (1982), flow regimes are mapped out for materials including minerals with respect to stress and temperature. These maps, much like phase diagrams, indicate the rate controlling flow process for the given environment. Figure 9 illustrates a deformation map for MgO. Mechanisms such as dislocation glide-controlled plasticity, power-law creep, and diffusion creep govern different regions. Each regime is enumerated by lines representing strain rates ranging from 1 to 10^{-10} s^{-1} . These lines indicate the strain rate for the particular temperature–stress state. One also sees the manner of the extrapolation of experimental high strain rate data (10^{-6}) to the earth conditions (10^{-15}) as long as the deforming process remains the same. At high stress, the flow is controlled by glide where the periodic atomic lattice forces resist dislocation motion. This is often referred to as the Peierls stress region. Here, the stress is high enough to overcome obstacles and the activation energy includes a term involving the deviatoric stress. As the stress decreases, the obstacles begin to dominate, creating a region where the flow stress is relatively insensitive to either temperature or strain rate. Power-law dislocation creep dominates where T is high enough for recovery processes to overcome the obstacles. At low stress and high temperature, diffusion comes into play. In the diffusion creep region, plasticity is accomplished by movement of atoms, either through the grain or along grain boundaries.

Another mechanism, dynamic recrystallization, appears at the high-temperature end of the map and is embedded in the dislocation creep regime. Here, flow is controlled by the growth of stress-free grains over stressed grains. Dynamic recrystallization may occur throughout the deformation map, but is not the dominant process in most of this region. It can assist other mechanisms by removing the high stress grains or the dislocation-riddled grains. It has long been thought to be active in Earth based on observations from natural rocks. Dynamic recrystallization is unique in that it may alter the grain size, thus moving a stress–temperature point from a field dominated by power-law creep to one dominated by diffusion. De Bresser et al. (1998, 2001) postulate that dynamic recrystallization will evolve the grain size for a given stress–temperature, so that the boundary between diffusion creep and power-law creep lies on the stress–temperature point.

2.14.3.7 Dislocations, Slip Systems, and Texture

The flow mechanism is defined by the behavior of the defects. It becomes expressed in the stress–strain rate relationship. A typical microscopic equation defining the steady-state flow process is as follows: flow rate = concentration of carrier $\times$ strength $\times$ velocity (Poirier, 1985). Dislocations, defined by their slip vectors, are controlled by atomic-scale forces. The manifestation of dislocation structures under the transmission electron microscope (TEM) reveals effects of the history of the mobile lattice defects. It further reflects the effects of the deforming conditions such as the pressure and temperature. The similarity between the dislocations of natural rocks and those of the experimentally deformed minerals provides sound arguments for the legitimacy of studying mantle rheology in the laboratory.

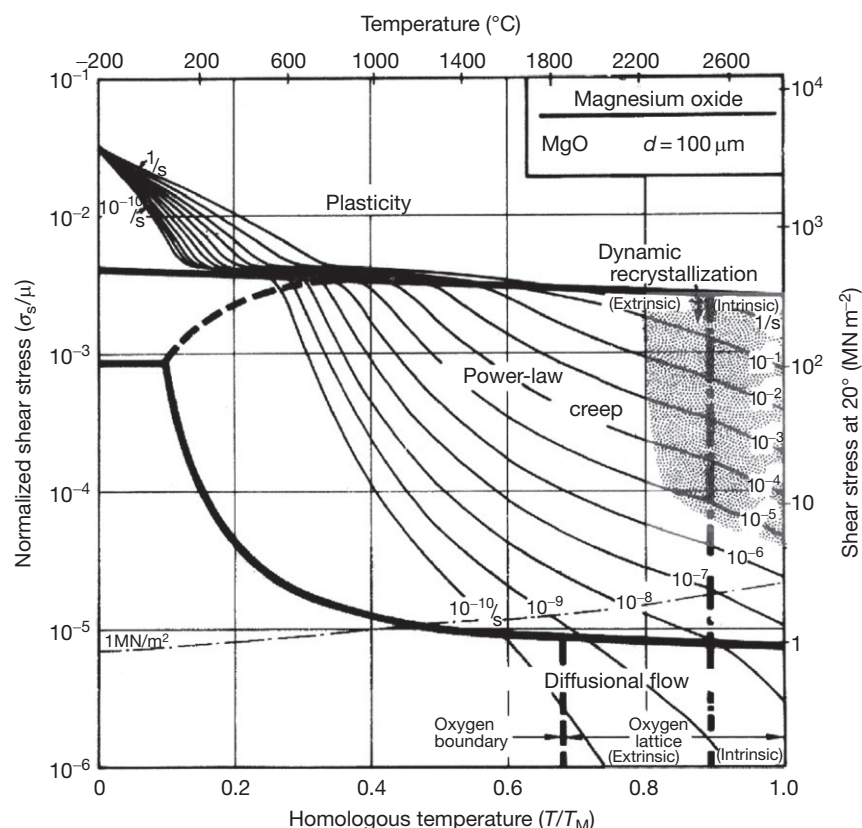


Figure 9 Deformation map of MgO from Frost and Ashby (1982). Dominant deformation mechanisms define different fields in this stress versus temperature space. The region labeled ‘plasticity’ is generally considered to be a region where dislocation glide is governed by the Peierls stress. Lines are drawn to represent fixed strain rates. Reprinted from Frost HJ and Ashby MF (1982) *Deformation-Mechanism Maps*. Oxford: Pergamon Press, with permission from Elsevier.

The study of dislocations of minerals using the TEM for samples that have been deformed at a known condition provides insights into the rheological behavior of the material (Cordier, 2002). Mantle minerals recovered from high-pressure experiments have been a recent research focus, including olivine (Couvry et al., 2004a; Li et al., 2006b), wadsleyite (Thurel et al., 2003), garnet (Cordier et al., 1996; Li et al., 2006a; Voegelé et al., 1998, 1999, 2000), stishovite (Cordier and Sharp, 1998), quartz (Cordier and Doukhan, 1995), and perovskite (Cordier et al., 2004). The slip systems of these minerals are characterized from the quenched samples, which were deformed at mantle pressure and temperature. These studies have enabled different views of the slip systems of minerals, for example, the discovery of the change in dominant high-temperature slip systems of olivine with pressure (Couvry et al., 2004a; Li et al., 2006b).

Even though TEM has been widely used in analyzing the dislocation structure of minerals, the examination of high-pressure phases is often challenging because some high-pressure phases are sensitive to electron beam damage. Recently, a new approach called large angle convergent beam electron diffraction (LACBED) has been employed to overcome this problem (Cordier, 2002). LACBED is a defocused diffraction method; it is friendly for beam sensitive materials and more reliable for providing information on burgers vectors than conventional

TEM. LACBED has been applied in the analysis of defects in many of the rock-forming minerals (Cordier, 2002).

While many insights relevant to Earth come from laboratory studies, at conditions far from those in nature, confirmation and predictive quantitative results await a theoretical basis. Theoretical approaches based on quantum mechanical models are being pioneered to simulate the dislocations in the minerals (Carrez et al., 2006; Cordier et al., 2005; Durinck et al., 2005a,b). One application is to calculate the energy of a crystal after a generalized stacking fault has been introduced by a rigid shift of a layer of atoms in the crystal along a shear plane. This approach provides insights into the effect of pressure on the plastic strain anisotropy, which is difficult to measure in the laboratory.

Dislocation flow can gradually cause the individual grains to rotate, with the result that the polycrystalline sample attains a preferred orientation (Wenk, 2002). When seismic waves travel through the regions of the earth with preferred orientations, velocity anisotropies are often observed (Silver, 1996; Tommasi, 1998) because minerals, such as olivine and pyroxene, are elastically anisotropic crystals. The relation between the fastest direction of the p wave and the flow direction has gradually been unveiled with the progress in our understanding of the slip systems of earth minerals (Mainprice and Humbert, 1994). Indeed, the pressure-induced transition of slip systems

in olivine, noted earlier, has been suggested as a cause of depth-dependent seismic anisotropy (Mainprice et al., 2005).

The preferred orientations (also called texture) of most mantle minerals have been investigated in the laboratory (Bascou et al., 2002; Couvy et al., 2004a,b; Merkel et al., 2002, 2003, 2004; Schafer et al., 1992; Wenk et al., 2004, 2005). Furthermore, a great deal of information from the texture obtained from samples that have experienced deformation under high P – T has been used to infer the rheological properties. A common method for analyzing the texture in a recovered sample is to collect an electron back-scatter diffraction pattern for a sample with a low dislocation density (Wright and Adams, 1992), using a scanning electron microscope.

In situ measurements using synchrotron x-ray and neutron sources have great potential for revealing the time-dependent development of texture. Both neutron and x-ray diffraction measure a bulk sample rather than surfaces and the measurement is carried out at a high P – T and a controlled strain rate. Synchrotron x-ray diffraction yields the quickest time resolution and also has the smallest scattering volume. Neutron diffraction collects data for more orientations and thus has more access to reciprocal space. For both x-ray and neutron diffraction, a density distribution of crystal orientations relative to the sample coordinates is then mapped out for samples that have been deformed under high pressures.

In parallel with the experimental work, theoretical approaches are also popular in modeling the texture in polycrystals formed during plastic deformation processes (Dawson and Wenk, 2000; Madi et al., 2005; Mainprice et al., 2005; Tommasi et al., 2000; Wenk et al., 1991, 2006). Models that have been widely used include viscoplastic self-consistent models (Clausen et al., 1998), the finite element model (Dawson, 2002; Dawson et al., 2001), and the Taylor model (Taylor, 1938). All models are based on the knowledge of the slip systems and flow equation of the crystals, as well as the link between each individual crystal and the aggregate polycrystal.

2.14.4 New Insights

2.14.4.1 Polycrystalline Materials

Rocks are invariably polycrystalline and normally polyphase. Understanding the rheological properties of the constituents does not necessarily mean that one can predict the properties of the aggregate. Tullis (2002) describes the complexity of the properties of crustal rocks and features attributable to the polycrystalline character. In general, the reported experimental data at crustal conditions on two phase rocks with high strength contrasts support the model in which the strength of the mixture falls between that of the end-member phases (Ji et al., 2001, 2003, 2004). Such models generally assume that the rheological properties of each phase in the mixture are the same as when it is a single phase deformed at the same condition (Takeda, 1998; Tullis et al., 1991). Bruhn et al. (1999) reported a weaker mixture than the two-end members (calcite and anhydrite), which have a similar strength, in which inter-phase boundary diffusion was reported as an import agent. Ford and Wheeler (2004) also demonstrated a theoretical

model on interface diffusion creep in which the behavior of a two-phase composite is completely different from that of the single-phase aggregates. Dresen et al. (1998) reported a stronger mixture that consists of 80% marble and 20% quartz and supported the model that predicts a higher strength with a lower porosity.

Even with the experimental observations described earlier, difficulties remain in quantifying the microstructure, stress, and strain within each phase in the composites. Various analytical models (Ji et al., 2001, 2003, 2004) and finite element models (Bao et al., 1991; Madi et al., 2005; Tullis et al., 1991) have been developed and they successfully predict the bulk strength of the composite from its end-members for different compositions and microstructures. However, because of the difficulty in detecting the behavior of the individual phases in the composite, these models are somewhat unconstrained. Furthermore, there are fewer experimental constraints on the rheology of aggregates at mantle conditions.

Diffraction-based determinations of stress usually yield multiple estimates of stress for each diffraction pattern, one for each diffraction line. Each diffraction line comes from a different population of grains within the sample. If there is more than one material making up the polycrystals, then each material usually contributes diffraction lines and, hence, measures of stress. Each subpopulation of grains that makes up a diffraction line shares a common orientation relationship within the sample, and, thus, a relationship of orientation relative to the applied stress field. This situation provides an unprecedented opportunity to investigate the heterogeneity of stress within the sample that is associated with these subpopulations. Previous measurements of force applied to an area of the polycrystalline sample yield only an average of the stress supported by the constituents. The relationship between these two types of measurements follows from some simple principles:

$$F_i = \int \sigma_{ij} dA_j \quad [4]$$

where F_i is the vector component of force, σ_{ij} is a component of the stress tensor, and A_j is a properly oriented area. Thus, the stress deduced from F/A may not be the stress at any point in the solid. The stress variation must satisfy the basic equilibrium equation

$$\sum_{j=1}^3 \frac{\partial \sigma_{ij}}{\partial x_j} = 0 \quad [5]$$

and maintain continuity of displacement. If the stress field within any grain is relatively constant, then eqn [2] becomes a sum over grains:

$$F_i = \sum \sigma_{ij} A_j \quad [6]$$

where the sum is over grains that define a continuous plane within the sample. In this view, the different subpopulations of grains may take on independent, and different, values of stress. The variation of stress required by eqn [3] would be represented as a broadening of the diffraction peaks, but the stress levels would reflect the properties of the grain. Grain to grain variation of stress may occur if the different subpopulations

have different strengths. Within the deformation field, no grain will support a greater stress than its strength. Thus, a composite of grains with different strengths could be expected to have subpopulations with different stresses. Here, we give two examples of this effect. The first is for a two-phase aggregate, as reported by Weidner and Li (2006).

A mixture of spinel (MgAl_2O_4) and MgO is demonstrated. We focus on data obtained during plastic flow of composites with volume distributions of 100% MgO (mgo100), 75% MgO/25% spinel (mgo75sp25), 25% MgO/75% spinel (mgo25sp75), and 100% spinel (sp100). The composites were studied in two experimental deformation runs using a DDIA, the first two samples in one run and the second two samples in the other run. As illustrated in Figure 10, two cylindrical samples are stacked along the unique stress axis, with metal foils separating the samples and also between the sample and the corundum end piston.

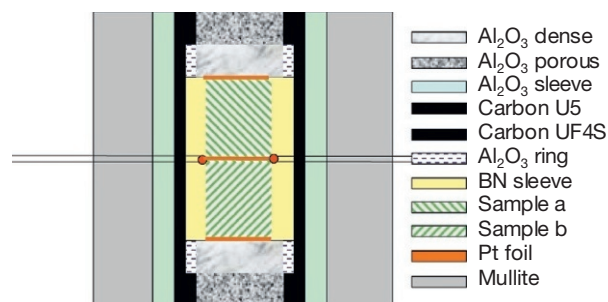


Figure 10 Illustration of a sample cell for two samples (a and b). This cell allows comparative studies of two materials. The one with the largest strain rate is generally the weakest as the stresses will be quite similar for the two samples.

Differential stress is measured from the energy-dispersive diffraction patterns recorded at 0° and 90° relative to the uniaxial compression direction (Li et al., 2004a,b). Plastic strain as a function of time is defined from sample images (Li et al., 2003; Vaughan et al., 2000). Samples were initially compressed to 5 GPa, then annealed at 1000°C for tens of minutes, and finally deformed at a strain rate of 10^{-5} s^{-1} for 10's of percent strain; the temperature was then lowered to 800°C where deformation continued. Then, the direction of the deformation was reversed, the sample being lengthened along the unique stress axis. Figures 11 and 12 illustrate the stress versus strain for the samples. The arrow labeled 1 indicates the point where the temperature was lowered to 800°C and the arrow labeled 2 indicates the reversal of the piston-loading direction. Stresses at 1000°C are near the uncertainty level of the measurement. Here, we focus on the 800°C data as it is robust and well resolved. Figure 13 summarizes the average loading stress for each material. The error bars indicate the spread of stress measurement based on different diffraction peaks. For spinel, the [400], [311], and [110] diffraction lines are used, while only the [200] line can be used for MgO because of the overlap of other lines with some of the spinel lines. As seen in Figure 13, the stress supported by spinel is nearly the same for the 100% spinel and the 75% spinel sample but much less for the 25% spinel sample. The stress in the MgO portion of the sample is nearly the same in all mixtures. Figure 11 illustrates that the 100% spinel and the 75% spinel, which were run in the same experiment, suffered a factor of two difference in strain even though the stress in the spinel was nearly the same. Thus, the addition of 25% MgO enabled considerably more deformation.

This combination of elastic stresses and strains can guide us to an improved understanding of the range of stress-strain properties that are likely. The large difference in stress between

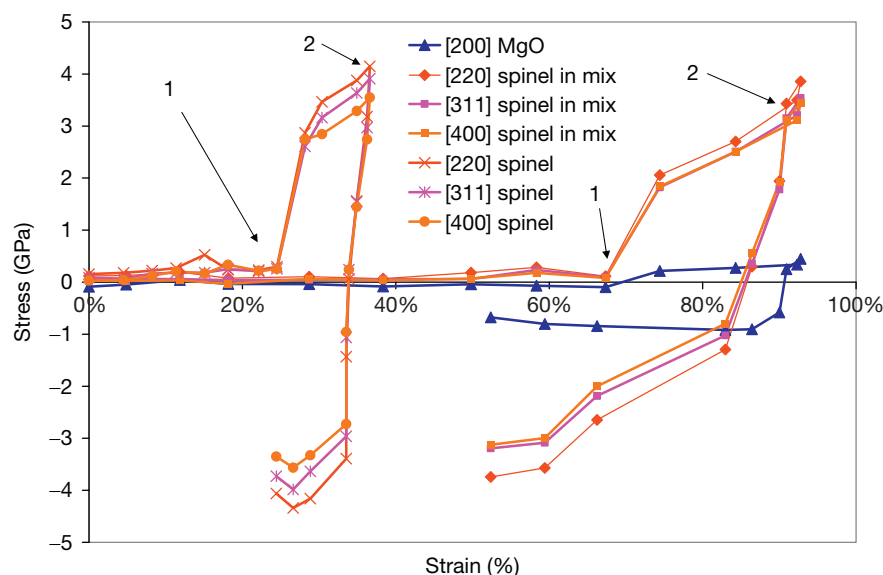


Figure 11 Stress as a function of plastic strain for two samples in the same cell. The set of curves to the right are the 75% spinel sample, deformed approximately twice the pure spinel sample. The arrow labeled 1 indicates the lowering of the temperature from 1000 to 800°C ; the arrow labeled 2 indicates the reversal of the loading force. Reproduced from Weidner DJ and Li L (2006) Measurement of stress using synchrotron x-rays. *Journal of Physics: Condensed Matter* 18: S1061–S1067.

the spinel grains and the MgO grains serves to illustrate that strong and weak grains can self-organize to allow the strong grains to support more stress. Even in the case of 25% spinel, we find that the stress in the spinel is about twice that of the MgO on the loading cycle. For the 75% spinel, the stress in the spinel is essentially the same as in the 100% spinel, and, thus, equal to the strength of the spinel sample. Still, the small amount of MgO present in this sample is responsible for the doubling of the plastic strain. In the 75% spinel sample, the MgO stress reversed sign during the extension portion of the experiment, while the spinel was still under compression. This illustrates that there would remain a significant residual stress in the sample if the loading force were simply removed at this time. However, on further extension, the spinel stress continued to grow to a similar magnitude, but reversed sign as on loading. In the sample with only 25% spinel, the stress in the spinel did not grow to its compressive magnitude during the extension phase of the experiment. Rather, it attained only the

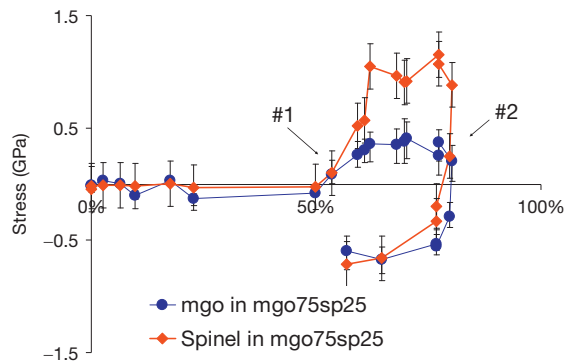


Figure 12 Stress as a function of plastic strain for the 25% spinel sample. The arrow labeled 1 indicates the lowering of the temperature from 1000 to 800 °C; the arrow labeled 2 indicates the reversal of the loading force. Reproduced from Weidner DJ and Li L (2006) Measurement of stress using synchrotron x-rays. *Journal of Physics: Condensed Matter* 18: S1061–S1067.

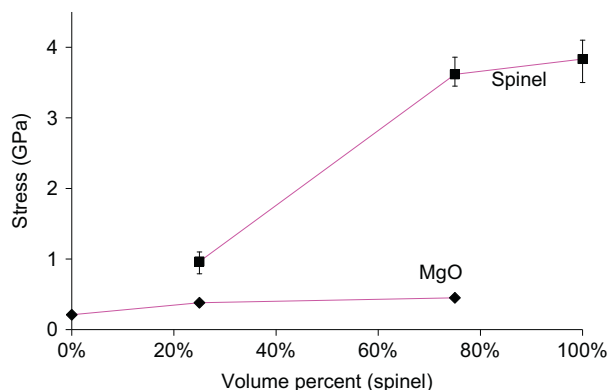


Figure 13 Average stress during loading at 800 °C for the two grain populations in a two-phase mixture as a function of volume percent of the spinel phase. The error bars indicate the range of stresses determined from the spinel diffraction peaks, [400], [311], and [220]. Only the MgO [200] peak could be used. Reproduced from Weidner DJ and Li L (2006) Measurement of stress using synchrotron x-rays. *Journal of Physics: Condensed Matter* 18: S1061–S1067.

stress value of the MgO portion of the sample. This indicates that upon loading, a fabric developed that enabled the strong phase to interact and support more of the stress. On the reversal of stress sign, this fabric did not allow the spinel to continue to support other spinel grains, and the stress in all the grains was limited by the strength of the MgO network. Thus, a significant fabric develops during the long loading cycle.

A second example of stress variations among subgrain populations comes from a monomineralic phase, MgO, in which different orientations have radically different strengths owing to the orientations of the weak slip planes (Li et al., 2004a,b; Uchida et al., 2004). Li et al. (2004a,b) report measurements of stress in an MgO sample at 500 °C. Figure 14 illustrates the measured stress using the [111] and [200] diffraction lines with several diffraction patterns as the sample is maintained at constant stress by the DDIA pressure system. One sample that was stressed at about two-third of the yield point exhibited a stress state that was the same for all diffraction lines. The sample that was stressed into yield experienced a 50% greater stress measured by the [111] diffraction lines than from the [200] diffraction lines. The difference in stresses between [111] and [200] is explained by plastic flow of MgO, for which the active slip systems required different critical resolved shear stresses and these systems are differently accessible to the different orientations of grains. The plastic strength parallel to [111] can be over an order of magnitude larger than the strength parallel to [100] (Paterson and Weaver, 1970). Thus, different populations of grains, which depend on the orientation in the polycrystals, support quite different levels of stress.

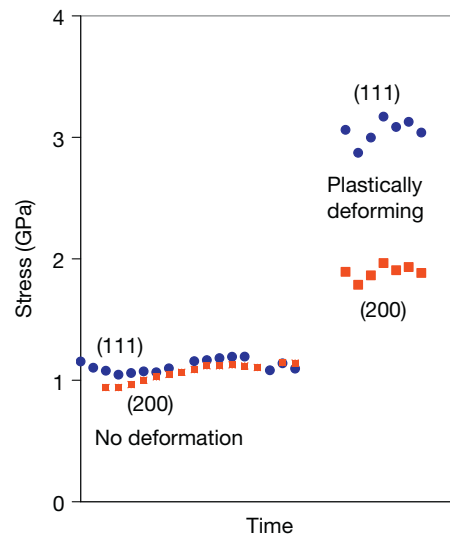


Figure 14 Differential stress in MgO samples at 500 °C during uniaxial loading in DDIA. The stress measured by two different diffraction peaks is illustrated by different colors. The higher stress sample plastically deformed plastically, while the low stress sample did not. The different points represent different diffraction spectra collected during the stress cycle. Adapted from Li L, Weidner D, Raterron P, Chen J, and Vaughan M (2004) Stress measurements of deforming olivine at high pressure. *Physics of the Earth and Planetary Interiors* 143–144: 357–367; Li L, Weidner DJ, Chen J, Vaughan MT, Davis M, and Durham WB (2004) X-ray strain analysis at high pressure: Effect of plastic deformation in MgO. *Journal of Applied Physics* 95(12): 8357–8365.

Different elastic moduli may also be responsible for generating different stresses in different subpopulations. By the same token, such elastic heterogeneity (or anisotropy for a monomineralic assemblage) may generate different strains within the different subpopulations. Such elastic strain anisotropy has been used to predict elastic modulus anisotropy in many studies using x-rays (Duffy et al., 1999; Kavner, 2003; Kavner and Duffy, 2001; Mao et al., 1998; Merkel et al., 2002). However, care must be exercised in these circumstances. As illustrated in the MgO example, strain anisotropy in a plastically deforming material likely reflects the plastic strength anisotropy of MgO rather than the elastic anisotropy.

2.14.4.2 Activation Volume of Olivine

The quantification of the rheological properties of mantle rocks at high pressure has been a task for scientists for more than half a century. The purpose is to provide a physical basis for understanding the dynamics of the mantle flow. Olivine, the major constituent of the upper mantle for the pyrolite composition, has remained the central focus because of its abundance and in part because of the limitations of the deformation apparatus and the measuring tools. It is one of the most studied minerals, and has been reported with a vast amount of information, from single crystal to polycrystal; from forsterite to fayalite; from super-dry to super-wet samples; from grain sizes of less than 0.5 μm to a few millimeters. With such intense attention, the results have converged. Yet, there are a few key variables that remain illusive.

As an illustration, we explore the issue regarding the activation volume (V^*) for which values from $<5 \text{ cm}^3 \text{ mol}^{-1}$ to larger than $27 \text{ cm}^3 \text{ mol}^{-1}$ have been reported from experimental work including those measuring the stress–strain rate relationship (Borch and Green, 1987; Green and Borch, 1987; Karato and Jung, 2003) and those measuring diffusivity of individual cations (Béjina et al., 1999). A small V^* and a large V^* will lead to different earth dynamic models as illustrated earlier, since a large V^* will magnify the effect of pressure on the strength of the mantle exponentially, with significant effects on mantle flow as well as earthquakes (Brodholt and Stein, 1988). A large activation volume for dislocation flow in the presence of a small activation volume for diffusion will lead to a change in the flow mechanism with depth (Karato and Wu, 1993), which may provide insight into why seismic anisotropy appears or disappears in the middle of the upper mantle.

The key to defining the effect of pressure on the flow of olivine is to determine the activation volume, V^* , by measuring the flow parameters over a large pressure range. Only the most advanced tools such as the DDIA or the rotational Drickamer apparatus (RDA) are capable of defining the stress–strain rate relation at pressures up to 15 GPa. Deforming olivine in these apparatus allow us to reach a pressure and temperature equivalent to that at the depth of 410 km in the earth even though we require a fast deforming process (strain rate of 10^{-5} s^{-1}), as a constant stress is applied. As mentioned earlier, we must rely on scaling laws to correct to Earth strain rates.

In defining the high-pressure flow of olivine, one needs first to identify the flow process that is active at the particular conditions. To map to mantle conditions, power-law creep is

the expected process. Power-law creep is characterized by thermal activation of processes that overcome obstacles of dislocation motion. The exponent, n , of eqn [1] is in the range of 3–5 while m is 0; that is, there is no grain size dependence. Competing processes include dislocation glide at a lower temperature and diffusion at a higher temperature and smaller grain size. Dislocation glide produces a much stronger dependence of strain rate on stress (an effective n would be >10). Dislocations will image as straight lines in TEM images. Diffusion will exhibit a positive value of m , thus expressing a grain size-sensitive flow process.

A series of papers (Durham et al., 2009; Girard et al., 2013; Kawazoe et al., 2009; Li et al., 2003, 2004a,b, 2006b; Raterron et al., 2009) explores the high-pressure flow of olivine. The early studies of Li et al. (2006b), using the DDIA, indicated very little increase in strength over a 10 GPa pressure range at 1200 °C, suggesting an activation volume of 0. However, infrared spectroscopy (IR) analysis of the recovered samples indicated the presence of small, but significant, amounts of water in the samples. Improvements in detection system (Weidner et al., 2010), development of a ‘dry’ sample cell (Durham et al., 2009), and an improved experimental protocol where flow is characterized at multiple pressures in a single experiment (Durham et al., 2009) have led to a refined value for activation volume. While Durham et al. (2009) report $V^* = 9.5 \pm 7 \text{ cm}^3 \text{ mol}^{-1}$, an extended data set that spans 1.5–8.7 GPa yields $V^* = 15 \pm 5 \text{ cm}^3 \text{ mol}^{-1}$ (Durham, private communication).

Girard et al. (2013) and Raterron et al. (2009) have focused on defining the rheological properties of single crystals with specific crystallographic orientations. They conclude that slip on the (010) crystallographic plane is dominated by displacements in the (100) direction at low pressure ($P < 8 \text{ GPa}$) and in the (001) direction at higher pressures, as also concluded by Couvy et al. (2004a). The cross-over results from an activation volume of $12 \pm 4 \text{ cm}^3 \text{ mol}^{-1}$ for the low-pressure slip system and $3 \pm 4 \text{ cm}^3 \text{ mol}^{-1}$ for the high-pressure system. Girard et al. (2013) further report that water weakens olivine, but the amount of weakening is not strongly affected by the amount of water. The lowered activation volume of the high-pressure system and the lowering of the strength owing to water provide a consistent data set, which includes Durham et al. (2009), Li et al. (2006b), and Raterron et al. (2009). Using the RDA apparatus, Kawazoe et al. (2009) concluded a slightly higher activation volume of $15\text{--}20 \text{ cm}^3 \text{ mol}^{-1}$.

2.14.4.3 High-Pressure Phases

High-pressure deformation experiments enable rheology measurements on high-pressure phases. Many meaningful state variable experiments can be carried out on metastable phases. Elasticity measurements sample the free energy function for small atom displacement. They are not sensitive to processes in which atoms are allowed to move relatively large distances. Flow, however, involves large displacements of the atoms, and the high temperature required to overcome obstacles will generally increase the kinetics to enable a phase transformation to the stable phase. Thus, high temperature flow for metastable phases is virtually unexplored.

Pyrope garnet is not stable at pressures below about 2 GPa. As a result, there are very few constraints on the flow properties

of this material despite its importance as a rock-forming mineral. Karato et al. (1995) estimated garnet rheology based on analogue studies. Measurements of the flow of other materials in the garnet structure, such as rare-earth garnets, taken with a scaling relation based on homologous temperature, can provide an informed estimate of flow properties. The primary assumption is that activation energy scales as T/T_m , where T_m is the melting temperature, among different compounds with the same crystal structure. This scaling equation leads to a picture of garnet that is significantly stronger than olivine.

Li et al. (2006a) used the DDIA to investigate the flow properties of a pyrope garnet and a pyrope-rich natural garnet. These measurements were made with a comparison to an olivine that would be chemically equilibrated with the garnet. Forsterite was found to be stronger than pyrope at 1200 °C, while San Carlos olivine was weaker than the natural garnet, with about 30% iron. Thus, iron is more significant in altering the rheological properties of olivine than of garnet. Furthermore, garnet is not significantly stronger than olivine under mantle conditions.

2.14.4.4 Phase Transitions Causing Elastic Softening

There are numerous phase transitions occurring with depth in Earth's mantle. Phase transition induces volume change. Volume change directly affects the effective bulk modulus K , since $1/K = \varepsilon/\sigma$, $\sigma = \delta P$, and $\varepsilon = \delta V/V$, with $\delta V/V$ being the total of elastic strain plus any volume change resulting from the phase transformation. Thus, $1/K_{\text{effective}} = \delta P/K_{\text{elastic}} + (\delta V_{\text{transformation}}/V)$, where $\delta V_{\text{transformation}}$ is the volume change of the system caused by the transformation that is driven by δP . If the phase transition has a characteristic time (τ) that is close to the seismic wave period ($2\pi/\omega$), peak attenuation and partial softening of seismic wave velocity should be observed. If $\tau \ll 2\pi/\omega$, then totally relaxed velocity and little attenuation should be observed. If $\tau \gg 2\pi/\omega$, unrelaxed velocity and little attenuation should be observed.

Li and Weidner (2008) and Weidner and Li (2009) examined the olivine–ringwoodite (Mg#30) phase transition during forced oscillation in the DDIA in the P , T conditions in the region of 8 GPa and 1300 °C. For this composition, because of its wide pressure range in the two-phase coexisting region, one can explore the possibility of applying a small mHz stress perturbation on a sample with coexisting olivine–ringwoodite to trigger the phase transitions. While the olivine phase exhibited normal elastic modulus (i.e., data reported using MHz frequency measurement tools), the effective Young's modulus of the olivine–ringwoodite mixture is significantly lower than an averaged elastic modulus value of the aggregate and the attenuation is high. Further characterization of the phase transition kinetics showed that the volume-changing phase transition is at a seismic period time scale. This suggests that phase transition-induced elastic softening may be an important mechanism affecting the seismic velocities. Figure 15 illustrates the effect of the transition on the attenuation when the driving period is close to the characteristic time of the transition. Driven at a 1000 s period, strain is plotted as a function of stress during a single cycle. Figure 15(a) is the observed signal when both phases coexist, while Figure 15(b) illustrates the same signal at a slightly different temperature where only one of the phases is stable. The area in the hysteresis loop indicates the amount of energy absorbed in a cycle. These experiments indicated that 1000 s is the approximate characteristic time of the phase transition, yielding the maximum energy absorption in a cycle.

2.14.4.5 Ferroelastic Phase Transition and Flip of Twinning State

Ferroelastic phase transitions are important processes for materials such as perovskite. Stress induces transformation from one twin state to another, a process that can consume energy and introduce a transformational strain, which may lower the elastic moduli. Figure 16 illustrates diffraction patterns taken as a function of time during a single stress cycle. The pattern

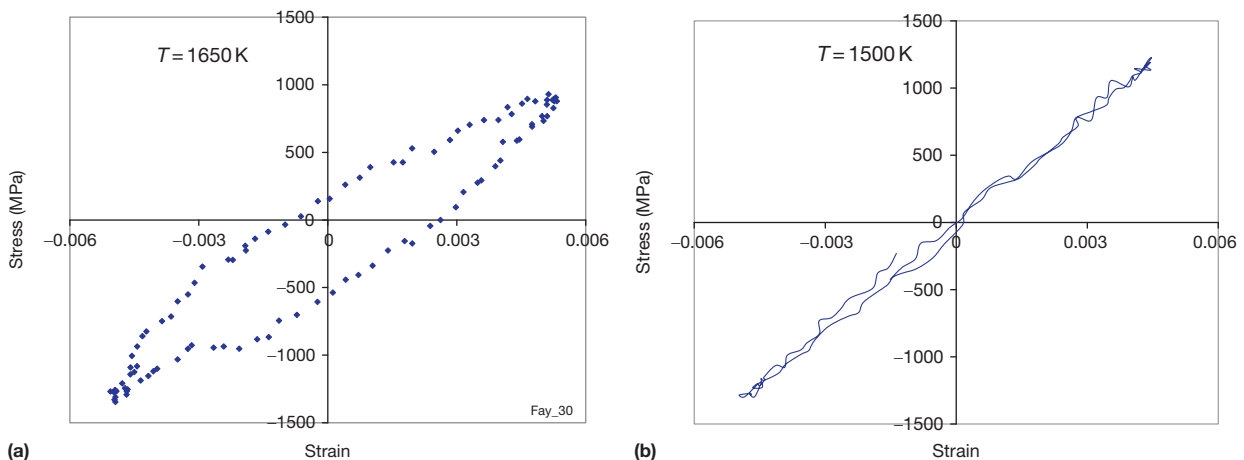


Figure 15 Stress versus strain for one cycle during a sinusoidal loading at a period of 1000 s. For (a), the temperature is 1650 K and both olivine and ringwoodite coexist in approximately equal amounts as demonstrated by x-ray diffraction. The resulting Q is about 5. For (b), the temperature is 1500 K and x-ray diffraction indicates that ringwoodite dominates the sample. The Q is indistinguishable from infinity. The area inside the hysteresis loop is the energy loss during one cycle. We conclude that the phase transition is responsible for the energy dissipation.

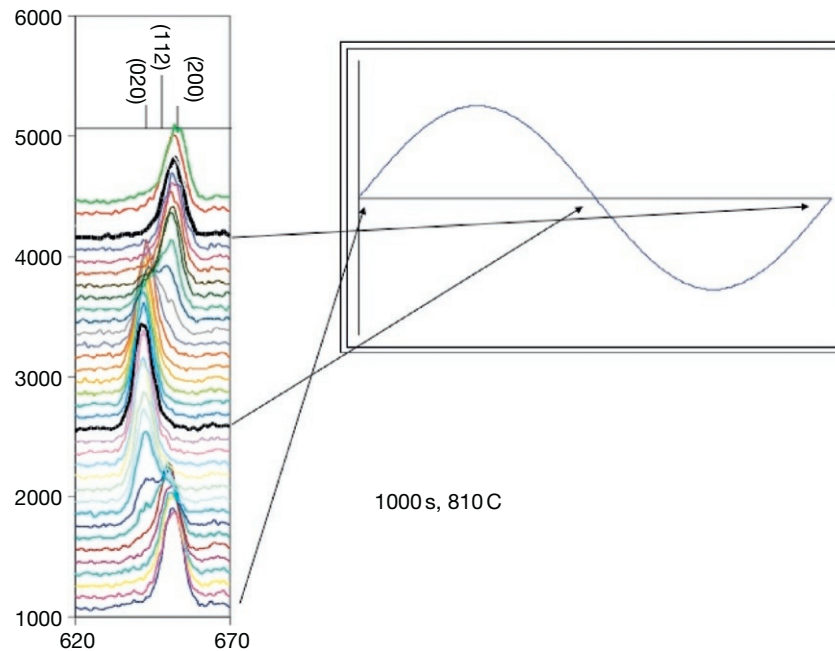


Figure 16 Several diffraction patterns, as a function of time, centered on the (020), (112), (200) triplet during a single stress cycle. The peak position, reflecting the lattice spacing, moves back and forth between the spacing for each of the three peaks.

illustrates the (020), (112), (200) triplet of the perovskite pattern for NaMgF_3 . Stress drives the structure between these three orientations through a twinning process. The change in lattice spacing as indicated by the position of the diffraction peak emphasizes the strain induced by the twinning process.

2.14.5 Conclusion

Recent breakthroughs driven by *in situ* characterization of high-pressure–high-temperature samples with synchrotron x-rays are changing the laboratory contribution to our understanding of the flow properties of Earth’s mantle. As of now, we are still on a strong growth curve for these capabilities. These new systems are now shedding light on a wide range of issues. The support of deviatoric stress in a polycrystalline material can be investigated with a new perception. The stress on sub-populations of grains can be directly observed. Deformation at high pressure is now observable. This has led to an understanding of the depth-dependent flow process, in terms of both the effect of pressure of individual phases and the flow process in high-pressure deep phases.

Future work promises new technical developments accompanied by significant advances in the field. Currently, the resolution of stress is about an order of magnitude lower than for low-pressure deformation experiments. Resolution can be improved with new detector/slit designs. A target of 10 MPa stress resolution at high pressure and temperature with data gathering times of a few minutes has been realized (Weidner et al., 2010). Higher pressure systems are surely coming. The initial stages of DDIA and RDA have been proven extremely successful at generating stress and pressure.

Following the design criteria, it should be possible to increase pressure to that at the top of the lower mantle. Opposed anvil devices stimulate a new range of possible systems that have the potential to generate conditions found in the middle of the lower mantle. In addition to quantitative flow laws, studies of flow-induced elastic anisotropy will be possible on all the mantle phases. The connection between geodynamics and seismology will be placed on a firm laboratory footing.

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2.15 The Ab Initio Treatment of High-Pressure and High-Temperature Mineral Properties and Behavior

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2.15.1 Introduction

The purpose of this chapter is to provide some examples about recent developments in the calculation of the high-pressure and high-temperature properties of materials using ab initio-based techniques, with the description limited to minerals under the relatively benign conditions of the center of the Earth. This chapter is not intended to review comprehensively all high-pressure and high-temperature ab initio calculations on minerals performed to date nor has the presumption to include the most significant ones. The few examples provided will only serve the purpose of showing what current ab initio techniques are capable of predicting.

With the word ‘ab initio,’ I refer here to those calculations based on the very basic laws of nature, in which no empirical adjustable parameter is used. Only fundamental constants of physics are allowed. Specifically, since we will be interested in the properties of matter, the relevant basic laws of physics are those describing the interactions between nuclei and electrons, that is, those of quantum mechanics. We shall see that

approximations to exact quantum mechanics are necessary to provide tools that can be used in practice; however, as long as these approximations do not involve the introduction of empirical parameters, we will still regard those techniques as ab initio.

I start the discussion by recalling the structure of the Earth, which can be broadly described in terms of three main shells. The outermost is the crust, with a thickness of only a few tens of kilometers, mainly formed by silicates. Below the crust, we find the mantle, which is customarily divided in an upper mantle and a lower mantle, separated by a transition zone. The mantle makes up most of the volume of the Earth, extending to a depth of 2891 km, almost halfway toward the center, and like the crust is also mainly formed by silicates and in particular by $\text{Mg}(\text{Fe})\text{SiO}_3$ with some significant fraction of $\text{Mg}(\text{Fe})\text{O}$ and SiO_2 . Below the mantle, we find the core, which is divided into an outer liquid core extending from 2891 to 5150 km depths and an inner solid core below that, down to the center of the Earth at 6346 km depth. It is widely accepted that the core is mainly formed by iron, possibly with some 5–10% of nickel,

plus a fraction of unknown light impurities, which reduce the density by 2–3% in the solid and 6–7% in the liquid with respect to the density of pure iron under the same pressure–temperature conditions.

Studying the high-pressure and high-temperature properties of the core- and mantle-forming materials is of fundamental importance to the understanding of the formation and evolution of our planet. In particular, knowledge of the thermal structure of the Earth and the thermoelastic properties of Earth-forming minerals will help us interpret and hopefully predict the behavior of the dynamic processes, which happen inside our planet, including the generation of the Earth's magnetic field through the geodynamo, and the convective processes in the mantle, which are ultimately responsible for plate tectonics, earthquakes, and volcanic eruptions.

The development of theoretical methods based on the very basic laws of nature of quantum mechanics (developed almost 90 years ago), coupled with the recent staggering increase of computer power (~500-fold in the past 10 years), has made it possible to approach the problem from a theoretical–computational point of view. When high-level first-principles methods are used, the results are often comparable in quality with experiments, sometimes even providing information in regions of the pressure–temperature space inaccessible to experiments.

The exact quantum mechanical treatment of a system containing a large number of atoms is a formidable task. The starting point of nearly every quantum mechanical calculation available is the so-called adiabatic approximation, which exploits the large difference of mass between the nuclei and the electrons. Since the electrons are much lighter, they move so much faster that on the timescale of their movement, the nuclei can be considered as fixed. Therefore, one solves only the electronic problem in which the nuclei are fixed and act as an external potential for the electrons. The energy of the electrons, plus the Coulomb repulsion of the nuclei, is therefore a function of the position of the nuclei and can act as a potential energy for the nuclei. This can be mapped in configuration space to create a potential energy surface, which can later be used to study the motion of the nuclei. Alternatively, forces can be calculated as the derivatives of the potential energy with respect to the position of the nuclei, and these can be used to move the atoms around, relax the system, solve Newton's equations of motion and perform molecular dynamics (MD) simulations, or calculate harmonic vibrational properties like phonons. The potential energy can also be differentiated with respect to the simulation cell parameters, which provides information on the stress tensor. The solution of the electronic problem also provides insights into the electronic structure of the system, which can be examined to study physical properties like bonding, charge distributions, magnetic densities, and polarizabilities.

Most first-principles studies of the high-pressure and high-temperature properties of Earth-forming materials are based on the implementation of quantum mechanics known as density functional theory (DFT). This is a technique that was introduced about 50 years ago by Hohenberg and Kohn (HK) (1964) and Kohn and Sham (KS) (1965) in an attempt to simplify the calculation of the ground-state properties of materials (in fact, later shown to be useful also for

finite-temperature properties; Mermin, 1965). The basic HK idea was to substitute the cumbersome many-body wave function of a system containing N particles, which is a function of $3N$ variables, with the particle density, which is only a function of three variables. The price to pay for this enormous simplification is a modification of the basic equations of quantum mechanics with the introduction of new terms, one of which, called exchange-correlation (XC) energy, is unfortunately unknown. However, KS proposed a simple form for the XC functional, known as the local density approximation (LDA) (Kohn and Sham, 1965), that would prove later as the insight that has made DFT so successful and so widespread today. More sophisticated XC functionals were developed in the following decades and are still being developed today, making DFT an evolving technique with increasingly higher accuracy. One additional attractive feature of DFT is the favorable scaling of computational effort with the size of the system. Traditional DFT techniques scale as N^3 , where N is the number of electrons in the system, but large effort is being put into the so-called $o(N)$ techniques, which for some materials already provide a scaling that is only directly proportional to the size of the system (Bowler et al., 2002; Soler et al., 2002).

A wide range of properties of minerals have been predicted using DFT techniques, like structural and electronic properties, phase diagrams, thermoelastic properties, speed of sound, transport properties, melting, solutions, and partitioning. In this chapter, we will focus only on a very limited number of applications.

The limitations in accuracy due to the current state of the art of DFT are expected to be progressively removed, either through the formulation of new XC functionals or with the developments of alternative techniques. Among these, dynamic mean field theory (Savrasov and Kotliar, 2003) and quantum Monte Carlo (QMC) (Foulkes et al., 2001) are probably the most promising on a timescale of 5–10 years.

After this introduction, the chapter is divided into two main sections. In the first, I will briefly review the main ideas behind first-principles simulations and in particular DFT and the pseudopotential (PP) approximation. I will also mention QMC techniques as promising advances beyond DFT. Section 2.15.3 will deal with the properties of materials, first at zero temperature and then at finite temperature. Techniques for the calculation of free energies will be presented, and this will be done by separating the low-temperature regime, where solids can be described within the quasi-harmonic approximation, from the high-temperature regime, where the technique of thermodynamics integration is introduced to calculate free energies. The calculation of melting curves and the thermodynamics of solutions will be presented as applications of these techniques. The final section includes recent calculations of the electrical and thermal conductivities of iron and iron alloys at the Earth's core conditions.

2.15.2 First-Principles Techniques

I begin this section by recalling the basic equation of quantum mechanics, the Schrödinger equation, which in the time-independent form is

$$\hat{H}\Psi = E\Psi \quad [1]$$

where $\hat{H}$ is the Hamiltonian of the system, E the total energy, and Ψ the many-body wave function, which is a function of the coordinates of the M nuclei $\{\mathbf{R}_i\}$ and the N electrons

$$\hat{H}(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_M; \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = -\sum_{i=1}^M \frac{\hbar^2}{2M_i} \nabla_{\mathbf{R}_i}^2 - \sum_{i=1}^N \frac{\hbar^2}{2m} \nabla_{\mathbf{r}_i}^2 + \frac{1}{2} \sum_{i,j=1; i \neq j}^M \frac{Z_i Z_j e^2}{4\pi\epsilon_0 |\mathbf{R}_i - \mathbf{R}_j|} + \frac{1}{2} \sum_{i,j=1; i \neq j}^N \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i=1}^M \sum_{j=1}^N \frac{Z_i e^2}{4\pi\epsilon_0 |\mathbf{R}_i - \mathbf{r}_j|} \quad [2]$$

where the first two terms are the kinetic energy operators for the nuclei and the electrons, respectively, with $\hbar$ the Planck's constant h divided by 2π and M_i and m the masses of the nuclei and the electrons, respectively. The third and the fourth terms in the equation represent the Coulomb repulsive energies between the nuclei and between the electrons, respectively, with Z_i the charges of the nuclei in units of e , the charge of the electron, and ϵ_0 the dielectric constant of the vacuum. The last term of the equation represents the electrostatic interaction between the electrons and the nuclei.

The only experimental input in the Schrödinger equation in the nonrelativistic approximation is the four fundamental constants: the Planck's constant h , the charge of the electron e , the mass of the electron m , and the dielectric constant of the vacuum ϵ_0 , which are the same for every system, plus the mass of the nuclei.

As mentioned in Section 2.15.1, solving the Schrödinger equation is essentially impossible for any real system more complicated than the hydrogen atom or more generally any system, which contains three or more quantum particles, and therefore, approximations are needed to make the problem manageable. The first approximation, which can be brought in, is the Born–Oppenheimer approximation, also called the adiabatic approximation. Here, one recognizes that the masses of the nuclei M_i are much larger than the mass of the electron m (the lightest possible atom is the hydrogen atom, which is almost 2000 times heavier than the electron), which therefore move on a much faster timescale. This means that, without much loss of accuracy for most systems, one can separate the electronic problem from that of the nuclei or in other words solve the Schrödinger equation for the electrons only, with the nuclei positions kept fixed. Therefore, we can rewrite eqn [1] as

$$\begin{aligned} \hat{H}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_M; \{\mathbf{R}_i\}) \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_M; \{\mathbf{R}_i\}) \\ = E\{\mathbf{R}_i\} \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_M; \{\mathbf{R}_i\}) \end{aligned} \quad [3]$$

where now the Hamiltonian depends only parametrically from the positions of the nuclei $\{\mathbf{R}_i\}$, and so do the wave function Ψ and the energy E . Once eqn [3] is solved, the energy $E\{\mathbf{R}_i\}$ can be interpreted as a potential energy for the motion of nuclei. At high temperature (above the Debye temperature), the quantum nature of the nuclei becomes negligible, and with essentially no loss of accuracy, one can treat their motion as they were classical particles. This allows to perform MD simulations, in which the Newton equations of motion for the nuclei are solved using the quantum mechanical forces evaluated from the derivative of $E\{\mathbf{R}_i\}$ with respect to the positions $\{\mathbf{R}_i\}$. If the quantum nature of the nuclei is important (e.g., hydrogen), this can be described using path integral techniques

$\{\mathbf{r}_i\}$: $\Psi = \Psi(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_M; \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$. If the system is isolated, in the nonrelativistic approximation, the Hamiltonian is given by

(Feynman, 1948; a very clear description of path integral methods can be found in Gillan (1990)).

2.15.2.1 Density Functional Theory

The introduction of DFT in 1964 by Hohenberg and Kohn (1964) tackled the many-body problem using a completely new approach. I will briefly outline here the main ideas of DFT; for an in-depth description of DFT, the reader may consult the original papers or the excellent books by Parr and Wang (1989) or Dreizler and Gross (1990) or the recent book by Martin (2004). A simplified (almost) nonmathematical explanation of DFT has been given by Gillan (1997).

Hohenberg and Kohn (1964) proved that the external potential V_{ext} acting on the electrons is uniquely determined (up to a trivial additive constant) by the electron ground-state density $n(\mathbf{r}) = \langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle = \int d\mathbf{r}_2, \dots, d\mathbf{r}_N |\Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2$, where Ψ is the ground-state wave function of the system and $\hat{n}(\mathbf{r})$ is the density operator. Here, we have omitted the dependence of Ψ from the positions of the nuclei for simplicity. Since $n(\mathbf{r})$ determines also the number of electrons N and since V_{ext} and N fix the Hamiltonian of the system, it turns out that the electron density completely determines all the electronic ground-state properties of the system and in fact, as shown later by Mermin (1965), also the finite-temperature properties.

One important property of the system is the energy, which can be written as

$$E[n] = F_{\text{HK}}[n] + \int V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \quad [4]$$

with

$$F_{\text{HK}}[n] = \langle \Psi[n] | \hat{T} + \hat{V}_{\text{ee}} | \Psi[n] \rangle \quad [5]$$

where $\hat{T}$ and $\hat{V}_{\text{ee}}$ are, respectively, the kinetic energy and the electron–electron interaction operators and $\Psi[n]$ is the ground-state wave function of the system. Note that $F_{\text{HK}}[n]$ does not depend on the external potential and therefore it is a universal functional. This is the crucial result of DFT. Using the variational principle, HK also proved that the ground-state density of the system is the one that minimizes $E[n]$ and the minimum of $E[n]$ is equal to the ground-state energy E_0 . The importance of these two results is clear; the only quantity that is needed is the electron density, no matter how many electrons are present in the system.

One year after the publication of the HK paper, KS invented an indirect method to solve the problem (Kohn and Sham, 1965). The idea is to write the energy functional as an easy part plus a difficult part:

$$F[n] = T_0[n] + E_H[n] + E_{xc}[n] \quad [6]$$

where $T_0[n]$ is the ground-state kinetic energy of an auxiliary noninteracting system whose density is the same as the one of the real system, $E_H[n]$ is the repulsive electrostatic energy of the classical charge distribution $n(\mathbf{r})$, and $E_{xc}[n]$ is the XC energy defined through eqn [6].

Minimizing the total energy $E[n]$ under the constraints of orthonormality for the one-particle orbitals of the auxiliary system, $\int \psi_i^*(\mathbf{r})\psi_j(\mathbf{r})d\mathbf{r} = \delta_{ij}$, one finds a set of one-particle Schrodinger-like equations:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}) \quad [7]$$

where the KS potential is

$$V_{KS}(\mathbf{r}) = V_{ext}(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{xc}(\mathbf{r}); \quad V_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} \quad [8]$$

and

$$n(\mathbf{r}) = \sum_i f(\varepsilon_i - \varepsilon_F) |\psi_i(\mathbf{r})|^2 \quad [9]$$

with $f(x)$ being the Fermi–Dirac distribution and ε_F the Fermi energy fixed by the condition

$$\int n(\mathbf{r}) d\mathbf{r} = N \quad [10]$$

These are the famous KS equations; they must be solved self-consistently because V_{KS} is a functional of the orbitals itself. The generalization to finite temperature is obtained by replacing E with the electronic free energy $U = E - TS$, where S is the electronic entropy, given by the independent-electron formula $S = -2k_B T \sum_i [f_i \ln f_i + (1 - f_i) \ln(1 - f_i)]$ with f_i being the thermal (Fermi–Dirac) occupation number of orbital i .

It is tempting to identify the single-particle eigenvalues ε_i with the energy of quasiparticles and therefore their distribution with the electronic density of states of the system. This would be conceptually wrong, as the KS eigenvalues are only an artificial mathematical tool to arrive at the ground-state density of the system. Nevertheless, it turns out that these DFT density of states often resemble very accurately the real density of states of systems, and they are therefore often used to analyze their electronic structure. However, it is important to remember that even if the exact XC functional $E_{xc}[n]$ were known, one should not expect the DFT density of states to be an exact representation of the real density of states of the system.

When self-consistency is achieved, the electronic free energy of the system is

$$U = \sum_{i=1}^N f(\varepsilon_i - \varepsilon_F) \varepsilon_i - \frac{1}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} + E_{xc}[n] - \int V_{xc}(\mathbf{r})n(\mathbf{r})d\mathbf{r} + E^{ion} - TS \quad [11]$$

where E^{ion} is the ionic electrostatic repulsion term. This would be the exact electronic free energy of the system if we knew $E_{xc}[n]$ (which also depends on temperature, though very little is known about this dependence). Unfortunately, the exact form of the XC (free) energy is not (yet) known.

2.15.2.1.1 Exchange correlation functionals

Kohn and Sham (1965) also provided an approximate expression for the XC functional, called the LDA. In the LDA, the dependence of functional on the density has the form

$$E_{xc}^{LDA}[n] = \int n(\mathbf{r}) \varepsilon_{xc}(n(\mathbf{r})) d\mathbf{r} \quad [12]$$

and $\varepsilon_{xc}(n)$ is taken to be the XC energy per particle of a uniform electron gas whose density is $n(\mathbf{r})$. This has been accurately calculated using Monte Carlo simulations (Ceperley and Alder, 1980) and parameterized in order to be given in an analytic form (Perdew and Zunger, 1981).

By construction, this approximation yields exact results if the density of the system is uniform and should not be very accurate for those systems whose density is highly inhomogeneous, for example, atoms and molecules. However, it turns out to work better than expected for a wide range of materials. In molecules, for example, the LDA usually overestimates the binding energies, but it yields in general good results for equilibrium distances and vibrational frequencies. It was the evidence of the very high quality of the LDA that has been the main responsible for the tremendous success of DFT.

Nowadays, a number of sophisticated functionals, like the so-called generalized gradient approximation (GGA) (e.g., Wang and Perdew, 1991) or the recently developed metaGGA (Staroverov et al., 2004; Tao et al., 2003), and hybrid functionals that contain a certain fraction of exact exchange according to various recipes (e.g., the B3LYP functional; Becke, 1993) have become available, but it is not obvious which one to prefer in general, with the good old LDA itself being competitive in accuracy in a variety of cases. It is also worth mentioning that, when used in combination with plane-waves methods (see Section 2.15.2.1.2), XC hybrid functionals usually require a computational effort that is orders of magnitudes higher than what is required by local XC functionals like the LDA or the GGAs. One of the main problems often ascribed to DFT is that it is difficult to incorporate dispersion interactions. Significant effort has been put in the last few years to correct XC functionals by adding dispersion corrections (e.g., Grimme, 2011; Tkatchenko et al., 2010 and references therein) or by developing new nonlocal functionals, which include dispersion interactions in the correlation energy (e.g., Lee et al., 2010; Klimeš et al., 2011 and references therein).

Whatever functional is used, these types of calculations all go under the classification of ab initio, in the sense that no experimental input is allowed, apart from the four fundamental constants mentioned in the preceding text. Of course, it would be desirable to have a unique functional with the highest possible accuracy for any system, but at the time of writing, we are not at this stage yet.

2.15.2.1.2 PPs and basis sets

In practical cases, it is often necessary to introduce one additional approximation in order to speed up the calculations, known as the PP approximation. In essence, this is a way to freeze the electrons of the core of the atoms and remove them from the calculations. The justification for doing this is that the core electrons are so tightly bound to the nuclei that they are essentially undisturbed by the chemical bonding, or

conversely, the chemistry of materials is unaffected by the behavior of the core electrons. This implies a saving in complexity and computer time, which is proportional to the number of electrons that have been frozen, but as we shall see in a moment, the saving becomes enormous in the most widely available computer codes, which are based on plane-wave expansions of the single-particle KS orbitals.

In order to solve the KS equations, it is necessary to expand the auxiliary KS orbitals in terms of some known basis functions. A variety of possible choices are available. Traditional quantum chemistry codes often use Gaussians, which are quite well suited for very localized orbitals, and in the course of the years, a large amount of expertise has accumulated to create high-quality basis sets for a wide range of materials. The drawback of Gaussians is that the quality of the basis set depends on the choice of the user, and transferability can be an issue when different systems are compared. An alternative set of functions, which are totally unbiased and systematically improvable, are plane waves. They also have the additional advantage of adapting naturally to calculations in which periodically boundary conditions are employed, which is a very useful set up even in systems, which have no periodicity, in order to reduce finite size effects. Plane-wave calculations are relatively simple, and the evaluation of forces and stress tensor is not much more difficult than the evaluation of the total energy. A drawback of plane waves is that a large number of them may be needed for describing rapidly varying functions, like the very localized core orbitals or the valence wave functions in the core region, which need to oscillate widely in order to be orthogonal to the core orbitals. For this reason, plane-wave calculations are almost always associated with the use of PPs.

The first aim of PPs is to eliminate the core electrons from the explicit calculations because they do not participate to the chemical properties of matter, at least until their binding energy is much higher than the energy involved in the chemical properties one wants to study. Hence, one freezes them around the nuclei and redefines the system as it was formed by ions plus valence electrons. We are left now with the problem of dealing with the oscillations in the core region of the valence wave functions, due to the orthogonalization to the core wave functions. The solution to this is the introduction of a PP, which substitutes the ionic Coulomb potential in such a way that the valence pseudoeigenvalues are the same as the all-electron (AE) ones on some reference configuration in the atom. The pseudo-wave functions coincide with the AE from a fixed core radius on and are as smooth as possible below the core radius, with the only constraint to be normalized (norm-conserving (NC) PPs). To satisfy these requirements, the PP usually must be angular momentum-dependent, that is, pseudo-wave functions corresponding to different angular momenta are eigenfunctions of different potentials. However, the long-range behavior of these different potentials must resemble the true one, because above the core radius, the pseudo-wave functions are identical to the AE ones. This means that the difference must be confined in the core region and then the PP can be written in the following form (Bachelet et al., 1982; Hamann et al., 1979; Kerker, 1980):

$$V_a(\mathbf{r}, \mathbf{r}') = V_a^{\text{loc}}(r)\delta(\mathbf{r}-\mathbf{r}') + \sum_{l=0}^{l_{\text{max}}} V_{a,l}(r)P_l(\hat{\mathbf{r}}, \hat{\mathbf{r}}')\delta(r-r') \quad [13]$$

where $V_a^{\text{loc}}(r)$ is the local long-range (spherical) part and approaches the AE potential above a cutoff radius r_c^{loc} , $V_{a,l}(r)$ are the short-range angular momentum-dependent part, the index a identifies the atom, and P_l is the projector onto the angular momentum l ,

$$P_l(\hat{\mathbf{r}}, \hat{\mathbf{r}}') = \sum_{m=-l}^{l^*} Y_{l,m}(\theta, \phi)Y_{l,m}^*(\theta', \phi') \quad [14]$$

with $Y_{l,m}$ being the spherical harmonics. The quality of the PP depends on its transferability properties, that is, the ability to reproduce the AE results over a wide range of electronic configurations, and of course the atom in different environments.

2.15.2.1.3 Ultrasoft (Vanderbilt) PPs

The requirement of norm conservation for the pseudo-wave functions can be a limiting factor for numerical calculations when also the valence electrons are very localized around their nuclei. This is a particularly serious problem for first-row elements, like carbon, and more so for nitrogen and oxygen and for transition metals, where the d -electrons are as localized as shallow-core states but have an extraction energy, which is not much larger than valence energies and for this reason cannot be excluded from the calculations. If this is the case, the utilization of NC PPs requires huge PW basis sets to achieve an acceptable accuracy. In a work published in 1990, Vanderbilt (1990) showed that, introducing a generalized formalism, the norm conservation constraint could be removed. In this way, one can construct much smoother pseudo-wave functions, with the only constraint of matching the AE at and above a fixed core radius (see Figure 1). The price to pay for having such smooth pseudo-wave functions is that, due to the fact that the pseudo-wave functions are not normalized anymore, the charge density has to be restored by adding an 'augmentation' part

$$n(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2 + n_{\text{aug}}(\mathbf{r}) \quad [15]$$

and the KS equations take the generalized form

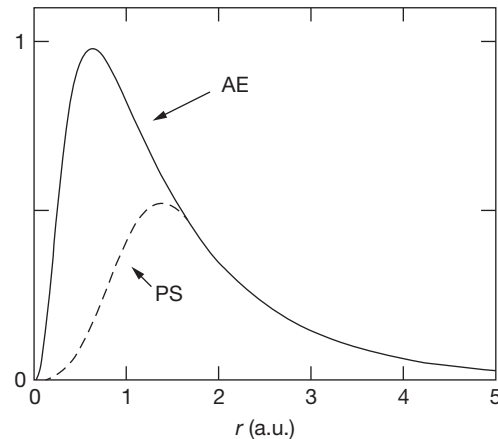


Figure 1 All-electron (solid) and ultrasoft pseudo (dashed)-radial wave functions of the 3d orbital of nickel. $r_c = 1.75$ a.u.

$$H_{KS}|\phi_i\rangle = \varepsilon_i S|\phi_i\rangle \quad [16]$$

where S is a nonlocal overlap operator.

2.15.2.1.4 The projector augmented wave method

In 1994, Blöchl invented a method to reconstruct the AE wave function inside the core region (Blöchl, 1994). The method, called projected augmented wave (PAW), is closely related to Vanderbilt's ultrasoft pseudopotential method, as shown by Kresse and Joubert (1999), but has been shown to be capable of reproducing essentially the same results of AE calculations, effectively removing the PP approximation. The PAW method is still only available in a handful of computer codes, but as evidences of its advantages accumulate, we believe that it will become a standard method of DFT-PW calculations.

2.15.2.2 Beyond DFT

As the search for the 'divine' functional in DFT goes on, alternative methods to solve the many-body problem are being developed, like the dynamic mean field theory (Savrasov and Kotliar, 2003) and QMC (Foulkes et al., 2001). The QMC method is particularly attractive because it adapts very well to parallel computers. As the speed of single-processor units approaches their physical limits, it is conceivable that the direction of the future increase of computer power will be the increase of the number of processors, and therefore, Monte Carlo methods will develop naturally on these machines. At the time of writing, the fastest computers in the world (e.g., Titan at Oak Ridge National Laboratory) already have more than 0.5 million processors working in parallel. Very few methods are capable of exploiting parallelism at this level efficiently; QMC is one of them.

QMC methods have been amply described in reviews (Foulkes et al., 2001), including detailed descriptions of how to implement them in practice (Foulkes et al., 2001; Umrigar et al., 1993). In the next section, I will briefly introduce the method and remand the reader to these reviews for more details.

2.15.2.2.1 QMC methods

QMC methods encompass a number of different techniques to solve the many-body problem of a system of N interacting quantum particles. In what follows, we will briefly mention the variational Monte Carlo (VMC) and the diffusion Monte Carlo (DMC) methods.

The VMC method gives an upper bound to the exact ground-state energy E_0 . Given a normalized trial wave function $\Psi_T(\mathbf{R})$, where $\mathbf{R}=(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ is a $3N$ -dimensional vector representing the positions of N electrons, and denoting by $\hat{H}$ the many-electron Hamiltonian, the variational energy $E_0 \equiv \langle \Psi_T | \hat{H} | \Psi_T \rangle \geq E_0$ is estimated by sampling the value of the local energy $E_L(\mathbf{R}) \equiv \Psi_T^{-1}(\mathbf{R}) \hat{H} \Psi_T(\mathbf{R})$ with configurations $\mathbf{R}$, distributed according to the probability density $\Psi_T(\mathbf{R})^2$. Common trial wave functions are of the Slater-Jastrow type:

$$\Psi_T(\mathbf{R}) = D^\dagger D^\downarrow e^J \quad [17]$$

where $D^\dagger$ and $D^\downarrow$ are Slater determinants of up-spin and down-spin single-electron orbitals and e^J is the so-called Jastrow factor, which is the exponential of a sum of one-body and

two-body terms (and possibly higher-order terms). The Jastrow factor is a parameterized function of electron separation, designed to satisfy the cusp condition, that is, to counterbalance the divergence in the potential when two electrons become very close, with a corresponding divergence in the kinetic energy of opposite sign. The parameters in the Jastrow factor are varied to minimize the variance of the local energy E_L , which also results in a minimization of the local energy itself. Several additional trial wave functions have also been used, including a more general form of that defined in eqn [17] in which one uses a linear combination of more than one Slater determinant or antisymmetrized geminals (Casula and Sorella, 2003).

Because of the variational principle, VMC results are an upper bound of true energy, which is not available in VMC (unless, of course, the trial wave function is the exact many-body wave function).

The DMC method is designed to obtain the true ground-state properties of the system. The basic idea is to compute the evolution of the many-body wave function Φ by the time-dependent Schrödinger equation in imaginary time $-\partial\Phi/\partial\tau = (\hat{H} - E_T)\Phi$, where E_T is an energy offset. If we consider only the kinetic energy in the Hamiltonian, the equation is equivalent to a diffusion equation, which allows Φ to be regarded as a probability distribution represented by a population of diffusing walkers. The potential term in the Hamiltonian makes the time-dependent Schrödinger equation in imaginary time equivalent to a rate equation, which is associated to a birth-death process of walkers in regions of low-high potential energy, respectively. It can be shown that, by adjusting the energy offset E_T appropriately, in the limit of imaginary time going to infinity, the distribution of walkers converges to the ground-state many-body wave function, and therefore, in principle, the DMC scheme yields the exact ground-state energy. However, for fermion systems, there is a fundamental problem. This is that Φ changes sign as $\mathbf{R}$ varies, so that it can only be treated as a probability in regions of $\mathbf{R}$ -space where it does not change sign. These regions and the nodal surfaces that define their boundaries have to be fixed by the introduction again of some trial wave function Ψ_T . The consequence of this is that the energy given by DMC is not the true ground-state energy, but again an upper bound because of the constraint that the nodal surface is that of Ψ_T . This gives rise to the so-called fixed-node error. The form of Ψ_T is usually the same as that used in VMC, and it is used to provide a starting point for DMC simulations.

An important issue in QMC simulations is the representation of the single-particle orbitals that make up Ψ_T . Much as in DFT, a number of different choices are possible, including Gaussians, plane waves, or B-splines (Alfè and Gillan, 2004a). The latter have the attractive feature of being intimately related to plane waves, sharing the properties of being unbiased and systematically improvable, but also being localized, a crucial property in QMC simulations.

It has also been shown recently that the evaluation and the storage of the trial wave function Ψ_T , often the most expensive part of the calculations, can be performed such that its cost scales linearly with the size of the system (Alfè and Gillan, 2004b; Manten and Lüchow, 2003; Roboredo and Williamson, 2005; Williamson et al., 2001), making the

so-called $o(N)$ -QMC techniques promising candidates for calculations on very large systems in the future.

The fixed-node error is the only uncontrollable source of error in DMC calculations; however, for systems containing atoms heavier than those of the first row, it is necessary to use PPs. The reason is that, for a trial wave function of fixed quality, the variance of the energy is proportional to the energy itself. Since core electrons have large negative energies, the variance associated to the evaluation of this component of the energy would mask completely the relatively small energies due to the valence electrons, which are those involved in the chemical bonding. For this reason, it is customary to use PPs also in QMC calculations. The nonlocality that is essential in these PPs gives rise to unavoidable errors in DMC. The reason is that the diffusion equation with a nonlocal Hamiltonian contains a term that can change its sign as time evolves and therefore presents the same difficulties as the fermion sign problem. To avoid this difficulty, one introduces the so-called localization approximation, in which this problematic term is simply neglected. If the trial wave function Ψ_T is close to the true (fixed-node) ground-state wave function Ψ , then this approximation introduces an error, which is small and proportional to $(\Psi_T - \Psi)^2$. This error, however, is nonvariational, so it can decrease and increase the total energy. Some recent promising work has gone toward addressing this problem (Casula et al., 2005, 2010).

To summarize, provided that all sources of technical errors are kept under control, the only two sources of error in QMC calculations are the fixed-node approximation and the locality approximation. It has been shown that DMC techniques can deliver much higher accuracy than DFT techniques (Binnie et al., 2010; Filippi et al., 2002; Grossman et al., 1995; Leung et al., 1999; Pozzo and Alfè, 2008; Santra et al., 2011; Tkatchenko et al., 2012), hinting that the aforementioned two approximations are less serious than those involved in the formulation of XC functionals in DFT calculations (at least for the systems considered). However, DMC total energy calculations are typically 4 orders of magnitude more expensive than traditional DFT techniques, and for this reason, the range of materials studied so far is rather limited, and therefore, so is the evidence that would favor DMC compared to DFT. As mentioned already in the preceding text, however, QMC techniques adapt naturally to large parallel computers (Towler et al., 2011), while traditional DFT techniques can take less advantage of this kind of architecture. It is expected therefore that the development and application of QMC techniques will be boosted in the future.

2.15.3 Mineral Properties and Behavior

Having introduced the computational tools, I now turn the discussion to the main purpose of this chapter, namely, how these tools can be applied to the study of the high-pressure and high-temperature properties of materials. I will focus in particular on the structure and elastic properties, phase diagrams, phase transitions, and thermodynamics of solutions.

To simulate materials under pressure is not much more difficult than to perform calculations at zero pressure; all it needs to be done is to change the volume of the simulation cell

appropriately. In doing so, one possible problem can be the shortening of the nearest-neighbor distance among the atoms, which, if it drops below the sum of the core radii of the PPs employed (or PAW-potentials), may affect the quality of the results. Therefore, some care is necessary in designing the potentials appropriate for the conditions where they need to be used. However, apart from this possible shortcoming, it is often the case that simulations at high pressure are even more accurate than those at low pressure. The reason is that as the pressure increases, the charge density becomes more homogeneous, which helps the XC functionals in their work.

By contrast, high-temperature simulations are much more demanding than the zero-temperature ones. The reason is that at high temperature, it is the free energy to play the essential role, and an accurate calculation of this requires expensive sampling of the phase space. For solids at not too high temperature, it is often accurate enough to use the quasi-harmonic approximation, in which the potential energy of the crystal is expanded to the second order in the displacement of the atoms away from their equilibrium positions. This quasi-harmonic potential usually provides a very accurate description of the dynamic properties of the system at low temperature and gives easy access to the free energy of the system, which can be calculated analytically as a function of temperature. The prefix 'quasi-' is there to indicate that this quasi-harmonic potential depends on the volume of the system. In practice, the quality of the thermodynamics obtained within the quasi-harmonic approximation is often preserved also to temperatures not far from the melting temperature, although at such high temperatures, a full account of anharmonic effects becomes necessary, at least to assess the validity of the quasi-harmonic approximation. For highly anharmonic solids and for liquids, one has to resort to MD or Monte Carlo techniques to sample the phase space. MD simulations are particularly attractive because they also provide dynamic information like diffusion or autocorrelation properties, which can be used together with the fluctuation-dissipation theorem to evaluate a number of physical properties of the system, as we shall see in the succeeding text. In the next section, we start by looking at the zero-temperature properties of materials, and in the following section, we turn to finite temperature.

2.15.3.1 Static Properties

2.15.3.1.1 Crystal structures and phase transitions

At zero temperature, the main thermodynamic variable is the internal energy of the system E . The simplest possible first-principles calculation one can do is the evaluation of the total energy of a system containing a certain number of atoms at fixed lattice sites. To find the most stable configuration of the atoms, one simply minimizes the total energy with respect to the atomic positions. This is usually done by evaluating forces, which are then used to move the atoms toward their equilibrium positions. For simple crystal structures, this could not be necessary, as the positions may be constrained by symmetry. An example of this is the Earth's mantle mineral MgO (periclase), which at zero pressure has a face-centered cubic crystal structure, with the Mg and O atoms in the primitive cell sitting at the corners and at the center of the

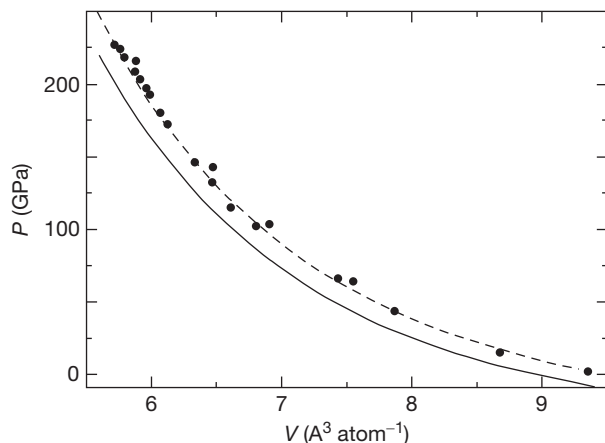


Figure 2 Pressure as function of atomic volume for rock salt MgO calculated with DFT-LDA (solid line) and DFT-GGA (dashed line), compared with experiments (stars) (Duffy et al., 1995). Calculations do not include zero-point or thermal effects. Reprinted from Alfè D (2005) *Physical Review Letters* 94: 235701, with permission. Copyright 2005 American Physical Society.

conventional cubic cell. In Figure 2, I show a comparison of pressures as function of volume between first-principles calculations and experiments. The calculations have been performed with DFT and both the LDA and the GGA approximations known as PW91 (Wang and Perdew, 1991) for the XC. The GGA results appear to agree very well with the experimental data, while the LDA one underestimates the pressure slightly. However, these particular calculations do not include zero-point motion and room temperature thermal expansion, which are instead present in the experiments. With those effects included (Karki et al., 2000), the experimental data would fall roughly in the middle of the two theoretical curves.

As the pressure is increased, the crystal structure of the material may change. For MgO, this does not happen up to at least 227 GPa (Duffy et al., 1995), but it is believed that as the pressure is increased still further, MgO would transform to the structure of CsCl, which is a simple cubic with the Mg and O atoms in the primitive cell still sitting at the corner and the center of the cube, respectively. The pressure at which the phase transformation occurs is defined by the point where the enthalpies of the two crystal structures cross. These enthalpies can be computed using ab initio techniques, by computing the energy E and the pressure p of the crystal as function of volume V , and then construct the enthalpy $H = E + pV$. For MgO, this has been done using a number of different techniques in the past, including various flavors of DFT (Chang and Cohen, 1984; Drummond and Ackland, 2002; Jaffe et al., 2000; Karki et al., 1997; Mehl et al., 1988; Oganov and Dorokupets, 2003; Oganov et al., 2003) and, very recently, QMC (Alfè et al., 2005). The latest DFT results point toward a transition at around 500 GPa, and the QMC results show that the transition is at 600 ± 30 GPa.

Another example of phase transition between different crystal structures is the transformation of iron from the zero-pressure magnetic body-centered cubic (bcc) to the hexagonal close-packed (hcp) structure at a pressure between 10 and

15 GPa (Jephcoat et al., 1986). Like the previous MgO case, the cubic structure is symmetrical, and it is necessary only to evaluate the energy of the crystal as function of volume. In contrast to bcc, however, the hcp crystal structure has an additional degree of freedom, coming from the lack of a symmetry relating the hexagonal plane and the direction perpendicular to the plane. This additional degree of freedom, known as the c/a ratio, needs to be optimized for every volume V . Once this is done, an enthalpy curve can be constructed and compared with that obtained from the bcc structure. Calculations using DFT with the LDA or various GGA's have been performed, and it has been shown that in this particular case, the LDA gives poor agreement with the experiments, even failing to predict the correct zero-pressure crystal structure (Cho and Scheffler, 1996; Körling and Häglund, 1992; Leung et al., 1991; Singh et al., 1991; Zhu et al., 1992), while PW91, for example, predicts the transition between 10 and 13 GPa (depending on the exact details of the pseudopotential or PAW potential) (Alfè et al., 2000a), in good agreement with the experimental value, which is in the range 10–15 GPa (Jephcoat et al., 1986).

Finally, as the last example, we mention the Earth's mantle mineral MgSiO_3 perovskite, which at mantle pressures has an orthorhombic crystal structure with the atoms in the cell not constrained by symmetry operations (D'Arco et al., 1993; Stixrude and Cohen, 1993; Wentzcovitch et al., 1993). It follows that at any fixed volume, one needs to optimize not only the lattice vectors but also the positions of the atoms in the cell. Very recently, this mineral has been found to display a phase transition to a new phase, named postperovskite (Murakami et al., 2004; Oganov and Ono, 2004). This transition has also been found by ab initio calculations (Iitaka et al., 2004; Oganov and Ono, 2004; Tsuchiya et al., 2004). The transition pressure from the static first-principles calculations appears to be ~ 100 GPa, which is below the core-mantle mantle pressure. However, Oganov and Ono (2004) and Tsuchiya et al. (2004) showed that high-temperature harmonic effects are responsible for an increase in the transition pressure, which is therefore predicted to be close to that at the top of D'' zone at the bottom of the mantle.

2.15.3.1.2 Elastic constants

Most of what we know about the interior of our planet comes from seismology and therefore from the elastic behavior of the minerals inside the Earth. The theory of elasticity of crystals can be found in standard books (Wallace, 1998), and therefore, we will not dwell on it for too long. Briefly, if a crystal is subjected to an infinitesimal stress $d\sigma_{ij}$, with i and j running through the three Cartesian directions in space, then it will deform according to the strain matrix $d\epsilon_{ij}$:

$$d\sigma_{ij} = \sum_{k,l} c_{ijkl} d\epsilon_{kl} \quad [18]$$

The constant of proportionality between stress and strain, C_{ijkl} , is a rank 4 tensor of elastic constants. With no loss of generality, we can assume $d\sigma_{ij}$ and $d\epsilon_{ij}$ to be symmetrical ($d\sigma_{ij} \neq d\sigma_{ji}$ would imply a nonzero torque on the crystal, which would simply impose an angular acceleration and not a deformation), and therefore, the elastic constant tensor is also symmetrical. It is therefore possible to rewrite the rank 2 tensors $d\sigma_{ij}$ and $d\epsilon_{ij}$ as six-component vectors, in the Voigt

notation, with the index pairs 11, 22, 33, 23, 31, and 12 represented by the six symbols 1, 2, 3, 4, 5, and 6, respectively. In this notation, the stress-strain relation appears as

$$d\sigma_i = \sum_j C_{ij} de_j \quad [19]$$

with i and j going from 1 to 6. Elastic constants are given as the coefficients C_{ij} in this notation. The matrix C_{ij} is symmetrical, so that the maximum number of independent elastic constants of a crystal is 21. Because of crystal symmetries, the number of independent constants is usually much smaller. For example, in cubic crystals, there are only three elastic constants; in hcp Fe, there are five; and in orthorhombic MgSiO₃ perovskite, there are nine.

Equation [19] provides the route to the calculation of the elastic properties of materials, and it can be applied at both zero and high temperatures. At zero temperature, the components of stress tensor can be calculated as (minus) the partial derivative of the internal energy with respect to the components of the strain:

$$\sigma_{ij} = -\partial E / \partial e_{ij} |_{\epsilon} \quad [20]$$

Examples of zero-temperature calculations of elastic constants include the DFT calculations of [Stixrude and Cohen \(1995\)](#) on the hcp crystal structure of iron at the Earth's inner-core conditions, which suggested a possible mechanism based on the partial alignment of hcp crystallites to explain the seismic anisotropy of the Earth's inner core. Other examples are the recent GGA and LDA calculations of the elastic constant of the recently discovered postperovskite phase by three groups ([Iitaka et al., 2004](#); [Tsuchiya et al., 2004](#); [Oganov and Ono, 2004](#); [Oganov et al., 2005](#)), which showed that this phase is elastically very anisotropic and that with a proper alignment, it is possible to explain the observed seismic anisotropy of the D'' region.

2.15.3.2 Finite Temperature

The extension to finite-temperature properties of materials could simply be obtained by substituting the internal energy E with the Helmholtz free energy F . The ij component of the stress tensor σ_{ij} is (minus) the partial derivative of F with respect to strain e_{ij} , taken at constant T , and holding all the other components of the strain tensor constant,

$$\sigma_{ij} = -\partial F / \partial e_{ij} |_{\epsilon, T} \quad [21]$$

Similarly, the pressure p is obtained as (minus) the partial derivative of F with respect to volume, taken at constant temperature:

$$p = -\partial F / \partial V |_T \quad [22]$$

If the system of interest is at sufficiently high temperature (above the Debye temperature), the nuclei can be treated as classical particles, and the expression of the Helmholtz free energy F for a system of N identical particles enclosed in a volume V and in thermal equilibrium at temperature T is ([Frenkel and Smit, 1996](#))

$$F = -k_B T \ln \left\{ \frac{1}{N! \Lambda^{3N}} \int_V d\mathbf{R}_1 \dots d\mathbf{R}_N e^{-\beta U(\mathbf{R}_1, \dots, \mathbf{R}_N; T)} \right\} \quad [23]$$

where $\Lambda = h / (2\pi M k_B T)^{1/2}$ is the thermal wavelength, with M being the mass of the particles and h being the Planck's constant; $\beta = 1 / k_B T$, k_B is the Boltzmann constant; and $U(\mathbf{R}_1, \dots, \mathbf{R}_N; T)$ is the potential energy function, which depends on the positions of the N particles in the system and possibly on temperature, in which case U is the electronic free energy. The multidimensional integral extends over the total volume of the system V .

By taking (minus) the derivative of F with respect to volume at constant temperature, we obtain

$$\begin{aligned} p(V, T) &= \frac{N k_B T}{V} + \frac{\int_V d\mathbf{R}_1 \dots d\mathbf{R}_N e^{-\beta U(\mathbf{R}_1, \dots, \mathbf{R}_N; T)} \left(\frac{-\partial U(\mathbf{R}_1, \dots, \mathbf{R}_N; T)}{\partial V} \right)_T}{\int_V d\mathbf{R}_1 \dots d\mathbf{R}_N e^{-\beta U(\mathbf{R}_1, \dots, \mathbf{R}_N; T)}} \\ &= \frac{N k_B T}{V} + \left\langle \left(\frac{-\partial U(\mathbf{R}_1, \dots, \mathbf{R}_N; T)}{\partial V} \right)_T \right\rangle \end{aligned} \quad [24]$$

The first term is the kinetic pressure and is present also in a system with no interactions between the particles (the ideal gas). The appearance of this term can be also understood by realizing that the integral appearing in eqn [23] is proportional to V^N . The second term is the canonical thermal average of the derivative of the potential (free) energy function with respect to volume, taken at constant temperature.

A similar expression holds for the stress tensor, which at finite temperature is evaluated as the thermal average of the derivative of F with respect to the strain components, plus the kinetic term.

Analogously, the internal energy $E = (\partial(F/T) / \partial(1/T))_V$ is given by

$$E(V, T) = \frac{3}{2} N k_B T + \langle U(\mathbf{R}_1 \dots \mathbf{R}_N; T) \rangle \quad [25]$$

This shows that a number of finite properties can simply be calculated by taking the thermal average of the corresponding quantity evaluated at $T=0$, plus a trivial kinetic term.

2.15.3.2.1 Molecular dynamics

If the system is ergodic, thermal averages (represented in the equations in the preceding text) can be calculated as time averages along an MD simulation ([Alder and Wainwright, 1959](#); [Gibson et al., 1960](#)). The main idea here is to move the ions according to the Newton's equations of motion. This is achieved in practice by discretizing the equation of motion $m_i \partial \mathbf{v}_i / \partial t = \mathbf{F}_i$ (m_i is the mass of atom i , $\mathbf{v}_i$ is its velocity, and $\mathbf{F}_i$ is the force acting on it). This is done by dividing time into time steps Δt and approximating the solution of the equation of motion, for example, as proposed by Verlet ([Allen and Tildesley, 1987](#); [Frenkel and Smit, 1996](#); [Verlet, 1967](#)):

$$\begin{aligned} \mathbf{r}_i(t + \Delta t) &= 2\mathbf{r}_i(t) - \mathbf{r}_i(t - \Delta t) + \frac{1}{m_i} \mathbf{F}_i(t) \Delta t^2 + o(\Delta t^4) \\ \mathbf{v}_i(t) &= \frac{\mathbf{r}_i(t + \Delta t) - \mathbf{r}_i(t - \Delta t)}{2\Delta t} + o(\Delta t^3) \end{aligned} \quad [26]$$

If the time step is small enough (usually less than 1/20 of a typical vibrational period), the Verlet algorithm conserves well the total energy of the system, on both short and long time-scales. If the volume of the simulation cell V and the number of

atoms N are kept constant, this so-called (N, V, E) simulation generates configurations in phase space that are distributed according to the microcanonical ensemble.

It is a standard result of statistical mechanics that thermal averages evaluated either in the microcanonical ensemble or in the canonical ensemble are equivalent if the system is sufficiently large, but it is useful to be able to perform simulations in ensembles other than the microcanonical one. For example, in order to obtain thermal averages in the canonical ensemble (i.e., constants N, V , and T), like the pressure in eqn [24], one can couple the system with an external heat bath, following the prescription of Andersen (Andersen, 1980), Nosé, or Hoover (Nosé, 1984; Hoover, 1985). When combined with the Parrinello–Rahman constant-stress technique (Parrinello and Rahman, 1980), this also allows simulations to be performed at constant T and $\sigma_{\alpha\beta}$ (see, e.g., Wentzcovitch et al. (1993)).

The forces F_i can be calculated within the framework of DFT, in which case the method is sometimes called first-principles molecular dynamics (FPMD). As mentioned earlier, for the method to be applicable in practice, one makes the fundamental approximation that the dynamics of the ions is decoupled from that of the electrons. This is usually justified due to the large difference in masses between the two sets of particles.

The first FPMD simulation was performed by Car and Parrinello (CP) in 1985 (Car and Parrinello, 1985), who proposed an elegant method to keep the electrons on the ground state along the MD trajectory. This was done by including the electronic degrees of freedom into a generalized Lagrangian, by assigning a fictitious mass to the single-particle wave functions and treating them as dynamic variables, like the positions of the ions. With a judicious choice of this fictitious mass, the electronic degrees of freedom would remain decoupled from the ionic ones, following them adiabatically while remaining in their ground state (at least for nonmetallic systems). An alternative method is to bring the electrons to the ground state at each time step (Kresse and Furthmüller, 1996), which is usually more costly than the CP scheme, but this is compensated by the possibility of making longer time steps. This method can be also easily applied to metallic systems and can become very efficient if combined with the extrapolation of the single-particle wave functions (Arias et al., 1992; Mead, 1992) and the electronic charge density (Alfè, 1999).

As some examples of the use of FPMD to compute thermal averages and study the high-temperature properties of solids, we mention the work of Oganov et al. (2001), who studied the high-temperature elastic constants of MgSiO_3 perovskite, and more recently that of Wookey et al. (2005), who studied the high-temperature elastic constants of MgSiO_3 postperovskite, and Gannarelli et al. (2005), who studied the elastic behavior of hcp iron at inner-core p and T conditions.

Using MD simulations, it is also possible to study the properties of liquids. For example, in a liquid, the atoms are free to diffuse throughout the whole volume, and this behavior can be characterized by diffusion coefficients D_α , where α runs over different species in the system. These D_α are straightforwardly related to the mean square displacement of the atoms through the Einstein relation (Allen and Tildesley, 1987):

$$\frac{1}{N_\alpha} \left\langle \sum_{i=1}^{N_\alpha} |\mathbf{r}_{\alpha i}(t_0 + t) - \mathbf{r}_{\alpha i}(t_0)|^2 \right\rangle \rightarrow 6D_\alpha t, \text{ as } t \rightarrow \infty \quad [27]$$

where $\mathbf{r}_{\alpha i}(t)$ is the vector position at time t of the i th atom of species α , N_α is the number of atoms of species α in the cell, and $\langle \rangle$ means time average over t_0 . The diffusion coefficient can also be used to obtain a rough estimate of the viscosity η of the liquid, by using the relation between the two stated by the Stokes–Einstein relation:

$$D\eta = \frac{k_B T}{2\pi a} \quad [28]$$

This technique was used by de Wijs et al. (1998) to estimate the viscosity of liquid iron at the Earth's core conditions. The Stokes–Einstein relation [28] is exact for the Brownian motion of a macroscopic particle of diameter a in a liquid of viscosity η . The relation is only approximate when applied to atoms; however, if a is chosen to be the nearest neighbors distance of the atoms in the solid, eqn [28] provides results that agree within 40% for a wide range of liquid metals. To calculate the viscosity rigorously, it is possible to use the Green–Kubo relation:

$$\eta = \frac{V}{k_B T} \int_0^\infty dt \langle \sigma_{xy}(t) \sigma_{xy}(0) \rangle \quad [29]$$

where σ_{xy} is the off-diagonal component of the stress tensor $\sigma_{\alpha\beta}$ (α and β are Cartesian components). This relation was used in the context of first-principles calculations for the first time by Alfè and Gillan (1998b), who first calculated the viscosity of liquid aluminum at ambient pressure and a temperature of 1000 K, showing that the method provided results in good agreement with the experiments and then applied the method to the calculation of the viscosity of a liquid mixture of iron and sulfur under the Earth's core conditions. In Figure 3, I show the integral in eqn [29] calculated from 0 to time t for this iron sulfur liquid mixture. In principle, this has to be

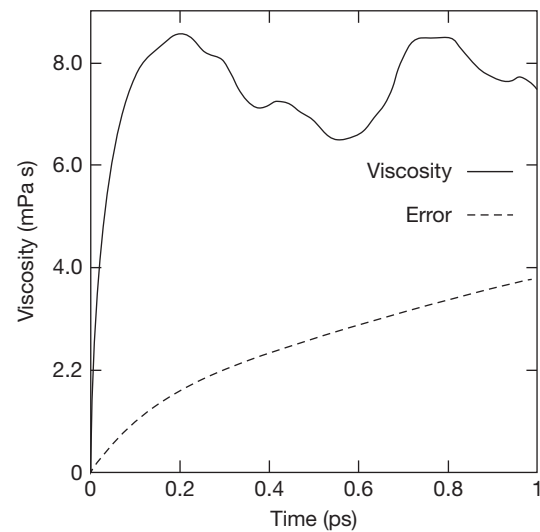


Figure 3 Viscosity integral of the average stress autocorrelation function and its statistical error as a function of time for liquid Fe/S under the Earth's core conditions. Reprinted from Alfè D and Gillan MJ (1998) *Physical Review Letters* 81, with permission. Copyright 1998 American Physical Society.

computed from zero to infinity, as stated in eqn [29]; however, in this particular case, there is nothing to be gained by extending the integral beyond about 0.2 ps, after which the integrand has decayed to zero and it is dominated by statistical noise. The figure also shows the computed statistical error on the integral, and from this, it was possible to infer the value for the viscosity $\eta = 9 \pm 2$ mPa s, in good agreement with that obtained from the diffusion coefficient via the Einstein relation [28], calculated to be $\eta \sim 13$ mPa s in a previous paper (Alfè and Gillan, 1998a).

2.15.3.3 Thermodynamic Properties

The phase stability of a system is determined by the minimum of its Gibbs free energy $G = F + pV$. Since $p = -\partial F/\partial V|_T$, knowledge of F as function of V and T allows the computation of G .

More generally, equilibrium in a multispecies system is determined by the chemical potentials μ_i , with i running over the different species, which represents the constant of proportionality between the energy of the system and the amount of the species i (Wannier, 1966):

$$\mu_i = \left(\frac{\partial E}{\partial N_i} \right)_{S,V} \quad [30]$$

where S is the entropy and N_i is the number of particles of the species i . Alternative equivalent definitions of the chemical potential are (Wannier, 1966; Mandl, 1997)

$$\mu_i = \left(\frac{\partial F}{\partial N_i} \right)_{T,V} = \left(\frac{\partial G}{\partial N_i} \right)_{T,p} = -T \left(\frac{\partial S}{\partial N_i} \right)_{E,V} \quad [31]$$

Equilibrium between two phases is determined by the condition of equality of the chemical potential of each individual species in the two phases. In the next section, I start the discussion by considering a single-component system. The extension to multicomponent systems will be considered in Section 2.15.3.3.5.

2.15.3.3.1 The Helmholtz free energy: Low temperature and the quasi-harmonic approximation

For a solid at low temperature, F can be easily accessed by treating the system in the quasi-harmonic approximation. This is obtained by expanding the potential (free) energy function U around the equilibrium positions of the nuclei. The first term of the expansion is simply the energy of the system calculated with the ions in their equilibrium positions, $E_{\text{perf}}(V, T)$ (this is a free energy at finite temperature, because of electronic entropy, and therefore depends on both V and T). If the crystal is in its minimum energy configuration, the linear term of the expansion is zero, and by neglecting terms of order three and above in the atomic displacements, we have that the quasi-harmonic potential is

$$U_{\text{harm}} = E_{\text{perf}} + \frac{1}{2} \sum_{lsz, l't\beta} \Phi_{lsz, l't\beta} u_{lsz} u_{l't\beta} \quad [32]$$

where u_{ls} denotes the displacement of atom s in unit cell l , α and β are Cartesian components, and $\Phi_{lsz, l't\beta}$ is the force-constant matrix, given by the double derivative $\partial^2 U / \partial u_{lsz} \partial u_{l't\beta}$ evaluated with all atoms at their equilibrium positions. This force-constant matrix gives the relation between the forces F_{ls}

and the displacements $u_{l't}$, as can be seen by differentiating eqn [32]:

$$F_{lsz} = -\partial U / \partial u_{lsz} = -\sum_{l't\beta} \Phi_{lsz, l't\beta} u_{l't\beta} \quad [33]$$

Within the quasi-harmonic approximation, the potential energy function U_{harm} completely determines the physical properties of the system, and in particular the free energy, which takes the form

$$F(V, T) = E_{\text{perf}}(V, T) + F_{\text{harm}}(V, T) \quad [34]$$

where the quasi-harmonic component of the free energy is

$$F_{\text{harm}} = k_B T \sum_n \ln(2 \sinh(\hbar w_n / 2k_B T)) \quad [35]$$

with w_n being the frequency of the n th vibrational mode of the crystal. In a periodic crystal, the vibrational modes can be characterized by a wave vector $\mathbf{k}$, and for each such wave vector, there are three vibrational modes for every atom in the primitive cell. If the frequency of the s th mode at wave vector $\mathbf{k}$ is denoted by $w_{\mathbf{k}s}$, then the vibrational free energy is

$$F_{\text{harm}} = k_B T \sum_{\mathbf{k}s} \ln(2 \sinh(\hbar w_{\mathbf{k}s} / 2k_B T)) \quad [36]$$

The vibrational frequencies $w_{\mathbf{k}s}$ can be calculated from first principles, and we shall see in the succeeding text how this can be done.

Once this quasi-harmonic free energy is known, all the thermodynamic properties of the system can be calculated. In particular, the pressure is given by

$$p = -\partial F / \partial V|_T = -\partial E_{\text{perf}} / \partial V|_T - \partial F_{\text{harm}} / \partial V|_T \quad [37]$$

The last term in the equation in the preceding text is the ionic component of the thermal pressure, and it is different from zero because the vibrational frequencies $w_{\mathbf{k}s}$ depend on the volume of the crystal. In fact, it is easy to see from eqn [36] that even at zero temperature, there is a finite contribution to the quasi-harmonic free energy, given by

$$F_{\text{harm}}(V, 0) = \sum_{\mathbf{k}s} \frac{\hbar w_{\mathbf{k}s}}{2} \quad [38]$$

This zero-point energy contribution to the harmonic free energy is also responsible for a contribution to the pressure. Since usually the vibrational frequencies $w_{\mathbf{k}s}$ increase with decreasing volume, these contributions are positive and are responsible for the phenomenon of thermal expansion in solids.

The dependence of $E_{\text{perf}}(V, T)$ on T also means that there is an electronic contribution to the thermal pressure, which is also positive, and in some cases (i.e., iron at Earth's core conditions) can be a significant fraction of the thermal pressure and a nonnegligible fraction of the total pressure (Alfè et al., 2001).

As an example of a calculation of the thermal expansivity of minerals using the quasi-harmonic approximation, I show in Figure 4 the temperature dependence of the thermal expansivity α of MgO at pressures up to 200 GPa, compared with experimental results. At ambient pressure, the first-principles $\alpha(T)$ agrees very closely with experiment up to ~ 1000 K (about

one-third of the melting temperature), which is a result of the good agreement of the calculated phonons with the experimental ones. The increasingly poor agreement at high T is due to anharmonic effects coming into play. These can be taken into account by avoiding the quasi-harmonic approximation and evaluating the full free energy of the system, as we shall see in [Section 2.15.3.3.3](#).

2.15.3.3.2 Calculation of phonon frequencies

There are two different first-principles strategies for calculating phonon frequencies. The method that is easier to understand starts from the fact that the force-constant matrix expresses the proportionality between displacements and forces, when the displacements are small enough for this relationship to be linear. All that has to be done in principle is to displace a single atom t in cell l' in Cartesian direction β , all other atoms being held fixed at their equilibrium positions; the forces F_{lsz} on all the atoms then give directly the elements of the force-constant matrix $\Phi_{lsz,l't\beta}$ for the given $(l't\beta)$. If this procedure is repeated for all other $(l't\beta)$, all the elements of the force-constant matrix can be obtained. Translational invariance implies that the number of separate calculations required to do this is at most three times the number of atoms in the primitive cell, but for most materials, symmetry relations can be used to reduce this number substantially. This strategy, sometimes called the small displacement method ([Kresse et al., 1995](#)), is implemented, for example, in the PHON code ([Alf , 2009a](#)). Although the small displacement method is widely used and can be very accurate, a word of caution is in order. Since DFT calculations on condensed matter always use periodic boundary conditions, the repeating cell must be large enough so that the elements $\Phi_{lsz,l't\beta}$ have all fallen off to negligible values at the boundary of the

repeating cell. This is readily achieved for some materials, particularly metals. However, in ionic materials, the force-constant elements fall off only as r^{-3} , and convergence can be slow. Moreover, in polar materials, the Coulomb forces produce a macroscopic electric field in the limit of zero wave vector. This electric field is responsible for a splitting in the frequencies of the vibrational modes parallel and perpendicular to the electric field (the so-called LO–TO splitting). This effect can be taken into account by adding a nonanalytic contribution to the dynamic matrix at wave vector $\mathbf{k}$, which has the form ([Giannozzi et al., 1991](#))

$$D_{sz,t\beta}^{\text{na}} = (m_s m_t)^{-1/2} \frac{4\pi e^2}{\Omega} \frac{(\mathbf{k} \mathbf{Z}_s^*)_{\alpha} (\mathbf{k} \mathbf{Z}_t^*)_{\beta}}{\mathbf{k} \epsilon^{\infty} \mathbf{k}} \quad [39]$$

where $\mathbf{Z}_s^*$ is the Born effective charge tensor for atom s , ϵ^{∞} the high-frequency static dielectric tensor, and m_s , m_t the mass of the atoms. These two quantities can be calculated in the framework of density functional perturbation theory ([Baroni et al., 1987, 2001; Giannozzi et al., 1991](#)) (DFPT), which also provides a second elegant strategy for the calculation of phonons in crystals. The main idea in DFPT, pioneered by [Baroni et al. \(1987\)](#), is to exploit the Hellmann–Feynman theorem to show that a linear order variation in the electron density upon application of a perturbation to the crystal is responsible for a variation in the energy up to second (in fact, third ([Gonze and Vigneron, 1989](#))) order of the perturbation. Using the standard perturbation theory, this linear order variation of the electronic charge density can be calculated using only unperturbed wave functions, which therefore only require calculations on the ground-state crystal. If the perturbation is a phonon wave with wave vector $\mathbf{k}$, calculation of the density change to linear order in the perturbation can be used to determine the force-constant matrix at wave vector $\mathbf{k}$. This can be done for any arbitrary wave vector, without the need of the construction of a supercell. The implementation of the method is by no means straightforward, and for further details, the reader should consult the original papers ([Baroni et al., 1987; Giannozzi et al., 1991](#)).

It should be pointed out, however, that free energies computed with the small displacement method converge very quickly to the thermodynamic limit with the size of the supercell, as demonstrated for the case of MgO in [Alf  \(2009a\)](#), even when LO–TO splitting is ignored. An additional advantage of the small displacement method is that it only requires the computation of forces and therefore does not need to be integrated into a first-principles code. Moreover, for large unit cells, the small displacement method is usually more efficient than DFPT.

As an example of first-principles calculations of phonon frequencies using the small displacement method ([Alf , 2009a](#)), I show in [Figure 5](#) the phonon dispersion relations for bcc iron under ambient conditions, compared with experimental data. We see that the agreement between theory and experiments is very good almost everywhere in the Brillouin zone, with discrepancies being at worst $\sim 3\%$.

Phonons can also be calculated at high pressure, and as an illustration of this, in [Figure 6](#), I show a comparison between DFT–GGA-calculated phonons, using the small displacement method ([Alf , 2009a](#)), and nuclear resonant inelastic x-ray scattering (NRIXS) ([Seto et al., 1995; Sturhahn et al., 1995](#))

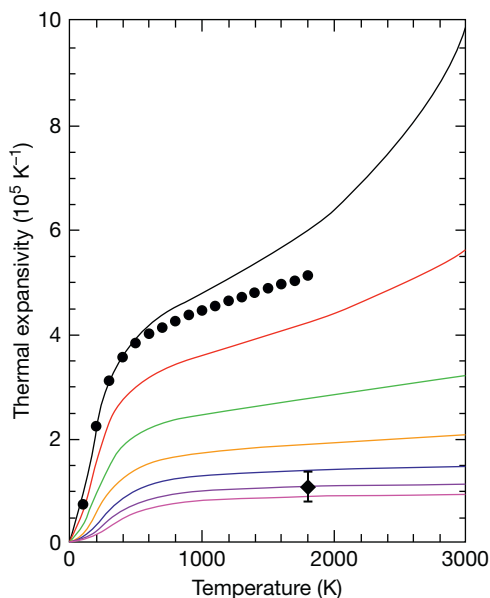


Figure 4 Temperature dependence of thermal expansivity α of MgO on isobars at 0, 10, 30, 60, 100, 150, and 200 GPa (curves from top to bottom). Experimental data at zero pressure are indicated by filled circles. Average value of α over temperature range of 300–3300 K and pressure range of 169–196 GPa derived from shock-wave experiments is indicated by the diamond.

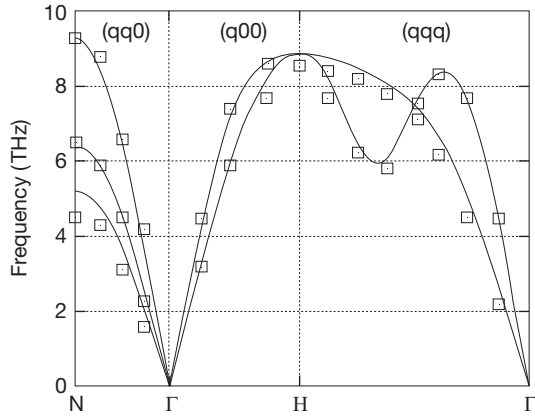


Figure 5 Phonon dispersion relations of ferromagnetic b.c.c. Fe. Lines and open squares show first-principles theory and experiment, respectively. Reproduced from Alfè D, Kresse G, and Gillan MJ (2000) *Physical Review B* 61: 132, with permission. Copyright 2000 American Physical Society.

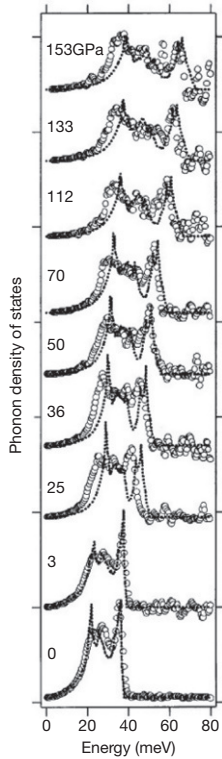


Figure 6 Phonon density of states of b.c.c. Fe (pressure $p=0$ and 3 GPa) and h.c.p. Fe (p from 25 to 153 GPa). Dotted curves and open circles show first-principles theory and experiment, respectively.

experiments, of phonon density of states of bcc and hcp iron from 0 to 153 GPa (Mao et al., 2001). The agreement between theory and experiments is good in the whole pressure region, being slightly better at high pressure.

The NRIXS technique has also been recently used to measure the partial density of states of FeS as a function of pressure (Kobayashi et al., 2004). Measurements were taken at pressures

of 1.5, 4.0, and 9.5 GPa, in the troilite, MnP-type, and monoclinic crystal structures of FeS, respectively, and were compared with first-principles calculations based on DFT-GGA. The agreement between the calculations and the experiments was reasonably good, although the FeS in the troilite structure was found to be unstable. The calculations were also used to provide the total density of states, which provided thermodynamic quantities such as the entropy and the specific heat.

2.15.3.3.3 The Helmholtz free energy: High temperature and thermodynamic integration

At high temperature, anharmonic effects in solids may start to play an important role, and the quasi-harmonic approximation may be not accurate enough. Moreover, if the system of interest is a liquid, the quasi-harmonic approximation is of no use. In this section, I shall describe a method to calculate the free energy of solids and liquid in the high temperature limit, provided that the temperature is high enough that the quantum nature of the nuclei can be neglected. If this is the case, the Helmholtz free energy F is defined as in eqn [23].

Performing the integral in eqn [23] to calculate F is extremely difficult. However, it is less difficult to calculate changes in F as some specific variables are changed in the system. For example, we have seen that by taking the derivative of F in eqn [23] with respect to volume at constant T , we obtain (minus) the pressure. Therefore, the difference of F between two volumes can be obtained by integrating the pressure p , which can be calculated using an MD simulation. Similarly, by integrating the internal energy E , one obtains differences in F/T .

It is equally possible to calculate differences in free energy between two systems having the same number of atoms N , the same volume V , but two different potential energy functions U_0 and U_1 . This can be done by introducing an intermediate potential energy function U_λ such that for $\lambda=0$, $U_\lambda=U_0$, and for $\lambda=1$, $U_\lambda=U_1$, and such that for any value of $0 < \lambda < 1$, U_λ is a continuous and differentiable function of λ . For example, a convenient form is

$$U_\lambda = (1 - f(\lambda))U_0 + f(\lambda)U_1 \quad [40]$$

where $f(\lambda)$ is an arbitrary continuous and differentiable function of λ in the interval $0 \leq \lambda \leq 1$, with the property $f(0)=0$ and $f(1)=1$. According to eqn [23], the Helmholtz free energy of this intermediate system is

$$F_\lambda = -k_B T \ln \left\{ \frac{1}{N! \Lambda^{3N}} \int_V d\mathbf{R}_1 \dots d\mathbf{R}_N e^{-\beta U_\lambda(\mathbf{R}_1, \dots, \mathbf{R}_N; T)} \right\} \quad [41]$$

Differentiating this with respect to λ gives

$$\frac{dF_\lambda}{d\lambda} = \frac{\int_V d\mathbf{R}_1 \dots d\mathbf{R}_N e^{-\beta U_\lambda(\mathbf{R}_1, \dots, \mathbf{R}_N; T)} \left(\frac{\partial U_\lambda}{\partial \lambda} \right)}{\int_V d\mathbf{R}_1 \dots d\mathbf{R}_N e^{-\beta U_\lambda(\mathbf{R}_1, \dots, \mathbf{R}_N; T)}} = \left\langle \frac{\partial U_\lambda}{\partial \lambda} \right\rangle_\lambda \quad [42]$$

and therefore, by integrating $dF_\lambda/d\lambda$, one obtains

$$\Delta F = F_1 - F_0 = \int_0^1 d\lambda \left\langle \frac{\partial U_\lambda}{\partial \lambda} \right\rangle_\lambda \quad [43]$$

This also represents the reversible work done on the system as the potential energy function is switched from U_0 to U_1 .

In most cases, a suitable choice for the function that mixes U_0 and U_1 is simply $f(\lambda) = \lambda$, and the thermodynamic formula [43] takes the simple form

$$\Delta F = F_1 - F_0 = \int_0^1 d\lambda \langle U_1 - U_0 \rangle_\lambda \quad [44]$$

This way to calculate free energy differences between two systems is called thermodynamic integration (Frenkel and Smit, 1996). The usefulness of the thermodynamic integration formula expressed in eqn [43] becomes clear when one identifies U_1 with the DFT potential (free) energy function and U_0 with some classical model potential for which the free energy is easily calculated, to be taken as a reference system. Then eqn [43] can be used to calculate the DFT free energy of the system by evaluating the integrand $\langle U_1 - U_0 \rangle_\lambda$ using FPMD simulations at a sufficiently large number of values of λ and calculating the integral numerically. Alternatively, one can adopt the dynamic method described by Watanabe and Reinhardt (1990). In this approach, the parameter λ depends on time and is slowly (adiabatically) switched from 0 to 1 during a single simulation. The switching rate has to be slow enough so that the system remains in thermodynamic equilibrium and adiabatically transforms from the reference to the ab initio system. The change in free energy is then given by

$$\Delta F = \int_0^{T_{\text{sim}}} dt \frac{d\lambda}{dt} (U_1 - U_0) \quad [45]$$

where T_{sim} is the total simulation time, $\lambda(t)$ is an arbitrary function of t with the property of being continuous and differentiable for $0 \leq t \leq 1$, $\lambda(0) = 0$, and $\lambda(T_{\text{sim}}) = 1$.

Thermodynamic integration can be used to calculate the free energies of both the solids and liquids. It is clear from eqn [43] that the choice of the reference system is almost completely irrelevant (of course, the stability of the system cannot change as λ is switched from 0 to 1), provided that ΔF can be calculated in practice. So, if the goal is to obtain ab initio free energies, it is essential to minimize the amount of ab initio work in order to make the calculations feasible. This is achieved by requiring that (i) the integrand in eqn [43] is a smooth function of λ , (ii) the thermal averages $\langle U_1 - U_0 \rangle_\lambda$ can be computed within the required accuracy on the timescales accessible to FPMD, and (iii) the convergence of ΔF as a function of the number of atoms N in the system is again achieved with N accessible to first-principles calculations. All points (i), (ii), and (iii) could obviously be satisfied by a perfect reference system, that is, a system that differed from the ab initio system only by an arbitrary constant. In this trivial case, the integrand eqn [43] would be a constant, and thermal averages could be calculated on just one configuration and with cells containing an arbitrary small number of atoms. The next thing close to a constant is a slowly varying object, and this therefore provides the recipe for the choice of a good reference system, which has to be constructed in such a way that the fluctuations in $U_1 - U_0$ are as small as possible. If this is the case, thermal averages of $U_1 - U_0$ are readily calculated on short simulations. Moreover, $\langle U_1 - U_0 \rangle_\lambda$ is a smooth function of λ , so a very limited number of simulations for different values of λ are needed and, finally, convergence of $\langle U_1 - U_0 \rangle_\lambda$ with respect to the size of the system is also quick. In fact, if the fluctuations in $U_1 - U_0$ are small enough, one can simply write $F_1 - F_0 \simeq \langle U_1 - U_0 \rangle_0$, with the

average taken in the reference system ensemble. If this is not good enough, the next approximation is readily shown to be

$$F_1 - F_0 \simeq \langle U_1 - U_0 \rangle_0 - \frac{1}{2k_B T} \langle [U_1 - U_0 - \langle U_1 - U_0 \rangle_0]^2 \rangle_0 \quad [46]$$

This form is particularly convenient since one only needs to sample the phase space with the reference system and perform a number of ab initio calculations on statistically independent configurations extracted from a long classical simulation.

Once the Helmholtz free energy of the system is known, it can be used to derive its thermodynamic properties. For example, it is possible to calculate properties on the so-called Hugoniot line and compare the results with those obtained in shock-wave experiments. The data that emerge most directly from shock-wave experiments consist of a relation between the pressure p_H and the molar volume V_H on the Hugoniot line, which is the set of thermodynamic states given by the Hugoniot–Rankine formula (Poirier, 1991):

$$\frac{1}{2} p_H (V_0 - V_H) = E_H - E_0 \quad [47]$$

where E_H is the molar internal energy behind the shock front and E_0 and V_0 are the molar internal energy and volume in the zero-pressure state ahead of the front. These experiments are particularly useful in identifying the melting transition. This is done by monitoring the speed of sound, which shows discontinuities at two characteristic pressures p_s and p_l , which are the points where the solid and liquid Hugoniots meet the melting curve. Below p_s , the material behind the shock front is entirely solid, while above p_l , it is entirely liquid; between p_s and p_l , the material is a two-phase mixture. To illustrate an example of the quality of the DFT–GGA predictions of the Hugoniot line, I show in Figure 7 the calculations of the $p(V)$ relation on the Hugoniot by Alf   et al. (2002a) for solid and liquid iron, compared with the experimental data obtained by Brown and

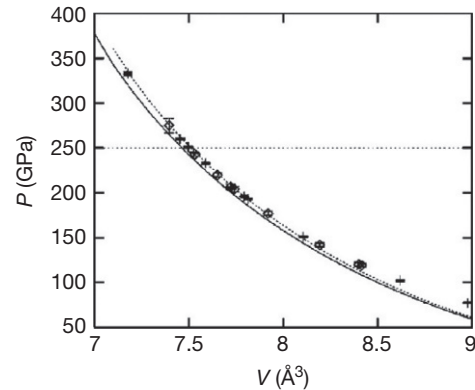


Figure 7 Experimental and first-principles Hugoniot pressure p of Fe as a function of atomic volume V . Symbols show the measurements of Brown and McQueen (1986). Solid curve is first-principles pressure obtained when calculated equilibrium volume of b.c.c. Fe is used in the Hugoniot–Rankine equation; dotted curve is the same, but with experimental equilibrium volume of b.c.c. Fe. The comparison is meaningful only up to a pressure of ca. 250 GPa (horizontal dotted line), at which point the experiments indicate melting. Reprinted from Alf   D, Gillan MJ, and Price GD (2002) *Physical Review B* 65: 165118, with permission. Copyright 2002 American Physical Society.

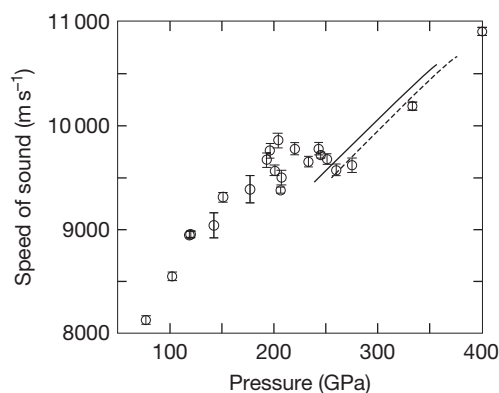


Figure 8 Longitudinal speed of sound on the Hugoniot. Circles, experimental values from [Brown and McQueen \(1986\)](#); continuous and dashed curves, present ab initio values without and with free energy correction (see text). Reprinted from [Alfè D, Gillan MJ, and Price GD \(2002\) *Physical Review B* 65: 165118](#), with permission. Copyright 2002 American Physical Society.

[McQueen \(1986\)](#). We can see that the agreement between the theory and experiments is extremely good. The two theoretical curves come from raw and free energy-corrected calculations (see the succeeding text). In [Figure 8](#), I show a comparison of the calculated speed of sounds of the liquid with those obtained in the shock-wave experiments. Again, the agreement between the two sets of data is extremely good.

2.15.3.3.4 Melting

The first to use thermodynamic integration in the context of first-principles calculations were [Sugino and Car \(SC\) \(1995\)](#), who calculated the Gibbs free energies G of solid silicon and liquid silicon at ambient pressure to obtain the DFT-LDA melting temperature T_m , given by the condition $G^l(T_m) = G^s(T_m)$, with superscript l and s indicating the liquid and solid, respectively. In their work, SC used a Stillinger-Weber potential ([Stillinger and Weber, 1985](#)) as reference system for both the solid and liquid, coupled with the scheme described in eqn [45] to compute free energy differences. They found that using a switching time T_m of < 1 ps was already sufficient to obtain a statistical accuracy on the free energies capable of predicting the melting temperature with an error of the order of 50 K. The importance of the SC work was that it showed that with a judicious choice of the reference system, these kinds of calculations are entirely accessible to first-principles techniques. The calculated LDA melting temperature of Si was 1350 K, about 20% lower than the experimental value (1680 K). Subsequent work showed that by using the GGA approximation, the calculated zero-pressure melting point was ~ 1500 K ([Alfè and Gillan, 2003](#)) and that by using the recently developed metaGGA ([Staroverov et al., 2004; Tao et al., 2003](#)), the results were very close to the experimental value ([Wang et al., unpublished.](#)). Shortly after the work of SC, de Wijs et al. used DFT-LDA in combination with thermodynamic integration to calculate the zero-pressure melting point of Al ([de Wijs et al., 1998](#)). They found the value of 890 K, in good agreement with the experimental value 933 K.

Encouraged by these early successes, DFT-GGA and thermodynamic integration were used by [Alfè et al. \(Alfè, 1999;](#)

[Alfè et al., 2001, 2002a\)](#) to calculate the free energies of solid and liquid iron under the Earth's core conditions, which they used to obtain a number of thermodynamic properties, including the whole melting curve in the region ~ 50 –400 K. They discovered that a simple sum of inverse power pair potentials of the form $U_{IP}(r) = B/r^\alpha$, where r is the distance between two ions and B and α are two adjustable parameters, did an excellent job in describing the energetics of the liquid and the high-temperature solid, provided that B and α were appropriately adjusted. As mentioned in the previous section, an additional crucial advantage of having a good reference system is that convergence of $F_1 - F_0$ with respect to the size of the system is very rapid, and in fact, for both solid iron and liquid iron, [Alfè et al.](#) found that already with 64-atom systems, $F_1 - F_0$ was converged to within better than 10 meV per atom, which in turn implied melting temperature converged to better than 100 K with respect to this single technical point. Their best estimate for the melting point at the inner-outer core boundary pressure of 330 GPa was $T_m = 6350 \pm 300$ K, where the error quoted is the result of the combined statistical errors in the free energies of the solid and liquid. Systematic errors due to the approximations of DFT are more difficult to estimate, and additional information can only be obtained when the problem is studied using a more accurate implementation of quantum mechanics. I will come back to this point later in the chapter.

At the present state of knowledge, the experimental understanding of the melting point of Fe under the Earth's core conditions is still scarce, as experiments based on diamond-anvil cells (DAC) cannot reach these pressures. Moreover, even in the region of the phase space where DAC experiments are possible, there is still considerable disagreement between different groups ([Boehler, 1993; Ma et al., 2004; Shen et al., 1998](#)) and between DAC and shock-wave experiments ([Brown and McQueen, 1986; Nguyen and Holmes, 2004](#)). However, the state of the art is improving, and very recently, two new DAC experiments have highlighted the difficulty of detecting the melting transition in older experiments ([Boehler, 1993](#)). [Jackson et al. \(2013\)](#) used synchrotron Mössbauer spectroscopy to monitor the dynamics of the iron atoms, and [Anzellini et al. \(2013\)](#) used x-ray spectroscopy to identify the onset on melting from the complete disappearance of peaks due to the presence of the solid from the spectrum. In particular, [Anzellini et al. \(2013\)](#) found that before melting, the system goes through a fast recrystallization process, at a temperature very close to that measured by [Boehler \(1993\)](#). They therefore suggested that this was the process detected in these older experiments ([Boehler, 1993](#)) and not melting. The results of [Anzellini et al. \(2013\)](#) agree very closely with the theoretical predictions of [Alfè et al. \(2002a\)](#).

On the theoretical side, I mention also the work of [Laio et al. \(2000\)](#) and [Belonoshko et al. \(2000\)](#), who performed DFT-based simulations to calculate the melting curve of Fe under the Earth's core conditions, although their approach was rather different from that of [Alfè \(1999\)](#) and [Alfè et al. \(2001, 2002a\)](#). Instead of calculating free energies, [Laio et al. \(2000\)](#) and [Belonoshko et al. \(2000\)](#) fitted a classical model potential to their first-principles calculations and then used the classical potential to compute the melting curve. To do so, they used the coexistence method, in which the solid and liquid are

simulated in contact in a box. This method is an alternative route to the calculation of melting curves and therefore equivalent to the free energy approach. However, Laio et al. and Belonoshko et al. found that at the pressure of 330 GPa, iron melted at 5400 and 7000 K, respectively. The reason of these large differences and the difference with the value 6350 K reported by Alfè et al. is due to the quality of the classical potentials employed and in particular to the free energy differences between these classical potentials and the DFT system. This was later investigated by Alfè et al. (2002b), who showed that it is possible to assess the differences in free energies between the classical potential and the DFT one and correct for it. In particular, it was shown that at a fixed pressure p , the first approximation of the difference T' in the melting temperature between the classical potential and the ab initio system is given by

$$T' = \Delta G^{\text{ls}}(T_{\text{mod}}) / S_{\text{mod}}^{\text{ls}} \quad [48]$$

where $S_{\text{mod}}^{\text{ls}}$ is the entropy of fusion of the model potential, T_{mod} its melting temperature, and $\Delta G^{\text{ls}} = (G_{\text{ab}}^{\text{l}} - G_{\text{mod}}^{\text{l}}) - (G_{\text{ab}}^{\text{s}} - G_{\text{mod}}^{\text{s}})$, where G is the Gibbs free energy; the subscripts 'ab' and 'mod' indicate the ab initio and the model system, respectively; and the superscripts 'l' and 's' indicate the liquid and solid, respectively. These differences of Gibbs free energies can be calculated using thermodynamic integration, which if the model potential is not too different from the ab initio, one can be calculated using the perturbative approach outlined in eqn [46] in the preceding text. The relation between ΔG , evaluated at constant p , and ΔF , calculated at constant V , is readily shown to be

$$\Delta G = \Delta F - \frac{1}{2} V \kappa_T \Delta p^2 + o(\Delta p^3) \quad [49]$$

where κ_T is the isothermal compressibility and Δp is the change of pressure when U_{mod} is replaced by U_{ab} at constants V and T . Once these corrections were applied, the results of Belonoshko et al. (2000) came in perfect agreement with those of Alfè et al. (2002a). These results are all displayed in Figure 9, together with a number of experimental data.

The coexistence method mentioned in the preceding text is an alternative route to the calculation of melting properties and as such delivers the same results if applied consistently. For its very nature, the method is intrinsically very expensive, because it requires simulations on systems containing a large number of atoms, typically many hundreds or even thousands. For this reason, until very recently, it had been only applied to calculations employing classical potentials. However, it has been recently shown that the method can in fact be applied also in the context of first-principles calculations. As computers become faster and faster, this method will become more and more common also within the context of first-principles calculations.

In Figure 10, I show the low-pressure melting curve of aluminum, as obtained by Vočadlo and Alfè with the free energy approach and the GGA XC potential (Vočadlo and Alfè, 2002) and, later, with the coexistence approach (Alfè, 2003), using the very same electronic structure techniques. This was the first time that the coexistence method was being applied using first-principles techniques. The simulations were performed on systems containing up to 1728 atoms, and the results showed that already, with modest system sizes of 512 atoms, the points calculated with the coexistence approach

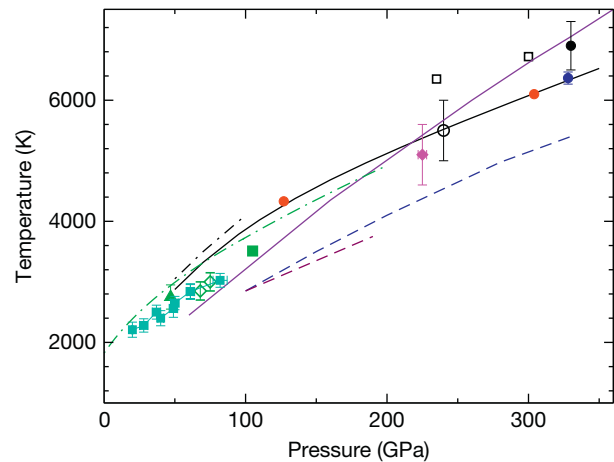


Figure 9 Comparison of melting curve of Fe from DFT calculations and experimental data. Black solid curve, first-principles results of Alfè et al. (2002a); blue-filled circle, first-principles coexistence result from Alfè et al. (2009b); red-filled circles, corrected coexistence results from Alfè et al. (2004); black-filled circle, QMC result from Sola and Alfè (2009); blue dashed curve, empirical potential results of Laio et al. (2000); purple curve, empirical potential results of Belonoshko et al. (2000); black chained and maroon dashed curves, DAC measurements of Williams et al. (1987) and Boehler (1993); green diamonds and green-filled square, DAC measurements of Shen et al. (1998) and Ma et al. (2004); magenta-filled squares, DAC measurements of Jackson et al. (2013); green chained curve: DAC measurements of Anzellini et al. (2013); black open squares, black open circle, and magenta diamond: shock-wave experiments of Yoo et al. (1993), Brown and McQueen (1986), and Nguyen and Holmes (2004). Error bars are those quoted in original references.

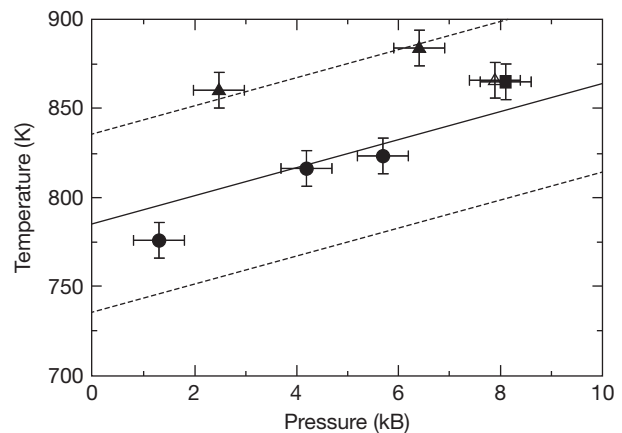


Figure 10 Temperatures and pressures at which liquid and solid Al coexist in first-principles simulations containing 1728 atoms (filled square), 1000 atoms (filled circles), and 512 atoms (filled triangles) performed using Γ -point sampling only. Open triangle is the result from a $2 \times 2 \times 1$ k -point grid on a 512-atom system. The solid line is the lower end of the melting curve calculated using the free energy approach in Vočadlo and Alfè (2002) (see text); light dashed lines represent error bars. Results from simulations using Γ -point sampling only for 1000- and 512-atom systems were reported in Alfè (2003).

differed from those obtained with the free energy approach by no more than 50 K. In fact, this difference was reduced even further if the 512-atom simulation was carried out with a denser k -point grid sampling, showing that genuine size effects

are very small already in systems containing 512 atoms. Note that the zero-pressure melting temperature of 786 K obtained with the GGA is not in very good agreement with the experimental value 933 K. It was argued (Vočadlo and Alfè, 2002) that the main cause of this discrepancy was a deficiency of the GGA of predicting the correct zero-pressure density, which comes out to be too large, and this would effectively correspond to calculating the melting temperature at a negative pressure. By applying a correction to the Helmholtz free energy in order to obtain the zero-pressure density for the solid and assuming that the same correction also applied to the liquid, they found that this corrected free energy predicted a zero-pressure melting temperature of 912 K, in excellent agreement with the experimental datum.

A short time after the coexistence work on aluminum, a second calculation using the same technique to calculate the melting curve of LiH appeared (Ogitsu et al., 2003) and more recently for the calculation of the melting curve of hydrogen up to 200 GPa (Bonev et al., 2004) and the melting curve of MgO in the pressure range 0–135 GPa (Alfè, 2005), reported in Figure 11. This last work was performed with both the LDA and the GGA exchange-correlation functionals, and despite that the results at high pressure were very similar, at zero pressure, the two calculations differed by about 20%, with the LDA being in good agreement with the experimental datum and the GGA predicting a lower melting temperature. This work also pointed out that the contribution of the electronic entropy to the free energy was nonnegligible and very different between the solid and liquid, such that it is responsible of a lowering of about 130(750) K of the melting temperature in the low(high)-pressure region of the phase diagram. This may be surprising, as solid MgO is a large band gap insulator, and indeed, a significant band gap remains in the high-temperature solid. However, the absence of local order in the liquid is such that the band gap is greatly

reduced, with a correspondingly significant increase of electronic entropy. In fact, recent experiments find that above 600 GPa, the electrical conductivity of liquid MgO increases significantly, suggesting that under these conditions, it becomes a metal (McWilliams et al., 2012). This emphasizes the need to accurately include electronic effects in the calculation of melting properties.

I now return to the melting point of iron at ICB pressures to describe two recent developments on the simulation side. Taking advantage of the large increase in computer power, I revisited the problem by performing a series of coexistence simulations using cells containing 980 atoms, using DFT. The simulations were performed at fixed cell lattice parameters, which results in slight nonhydrostatic conditions. To estimate both the effect of nonhydrostaticity and finite simulation cell size, I performed constant-stress simulation on much larger systems (7840 atoms) using an embedded atom model constructed to closely reproduce the energetics of iron at these conditions. The tests showed that nonhydrostaticity is responsible for an underestimate of the melting temperature by ≈ 100 K and finite size for an overestimate of ≈ 100 K, so that the two errors cancel each other. The simulation provided a melting point of 6370 ± 100 K at 328 GPa, which is on the melting curve obtained using the free energy approach (Alfè et al., 2002a). Around the same time, Sola and Alfè (2009) used QMC methods to investigate the accuracy of DFT at predicting the melting point of iron at the Earth's core conditions. This was done by computing free energy differences between QMC and DFT using the perturbative method described in eqns [46] and [48] in the preceding text. The calculations showed a slight increase of melting temperature to 6900 ± 400 K (the error corresponds to one standard deviation), which essentially confirmed the DFT prediction of a 'high' melting point of iron at the Earth's core conditions.

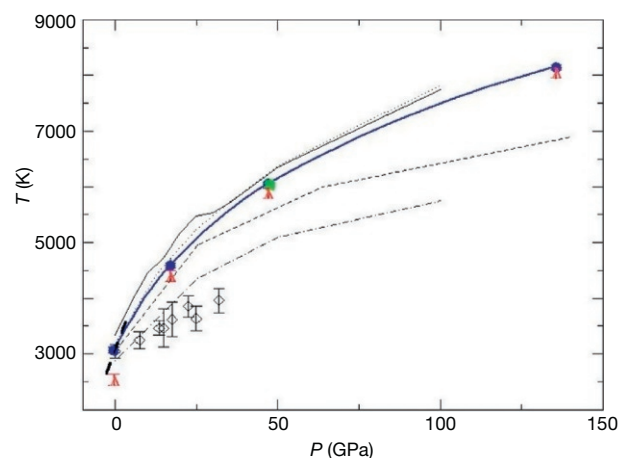


Figure 11 Melting curve of MgO obtained with DFT-LDA coexistence simulations performed on 432-atom cells (blue dots and heavy solid line), 1024-atom cell (green square), and DFT-GGA results (red triangles; Alfè, 2005), compared with experiments (open diamonds; Zerr and Boehler, 1994). Other curves show results of earlier modeling work based on interaction models. Reproduced from Alfè D (2005) *Physical Review Letters* 94: 235701, with permission. Copyright 2005 American Physical Society.

2.15.3.3.5 Solutions

I now turn the discussion to systems formed by more than one species of atoms. For example, consider two different substances and mix them together, and in general, they will form a solution, like sugar and coffee. I call solvent the substance present in the largest quantity (coffee) and solute the other (sugar). In general, solutions may have more than one solute and/or more than one solvent, but for simplicity, we will focus here only on binary mixtures.

In this section, I want to discuss how first-principles methods can be used to study the thermodynamic properties of solutions. As an example of the methods to be discussed, I will present calculations on iron alloyed with either sulfur or silicon or oxygen, at the conditions of pressure and temperature of the Earth's inner-core boundary, and how these calculations have been used to estimate the composition of the core. The techniques, however, are completely general and can be applied also to other systems under different thermodynamic conditions.

As mentioned in the preceding text, the behavior of solutions can be understood in terms of the chemical potential μ_i , defined in eqns [30] and [31]. Consider now a solution with N_A particles of solvent A and N_X particles of solute X, with $N = N_A + N_X$. In the high temperature limit, the Helmholtz free energy of this system is

$$F = -k_B T \ln \frac{1}{\Lambda_A^{3N_A} \Lambda_X^{3N_X} N_A! N_X!} \int_V d\mathbf{R}_1 \dots d\mathbf{R}_N e^{-U(\mathbf{R}_1, \dots, \mathbf{R}_N; T)/k_B T} \quad [50]$$

According to eqn [31], we have

$$\mu_X = \left(\frac{\partial F}{\partial N_X} \right)_{T,V} = F(N_A, N_X + 1) - F(N_A, N_X) \quad [51]$$

which can be evaluated using eqn [50]:

$$\mu_X = -k_B T \ln \frac{1}{\Lambda_X^3 (N_X + 1)} \frac{\int_V d\mathbf{R}_1 \dots d\mathbf{R}_N d\mathbf{R}_{N+1} e^{-U(\mathbf{R}_1, \dots, \mathbf{R}_N, \mathbf{R}_{N+1}; T)/k_B T}}{\int_V d\mathbf{R}_1 \dots d\mathbf{R}_N e^{-U(\mathbf{R}_1, \dots, \mathbf{R}_N; T)/k_B T}} \quad [52]$$

The ratio of the two integrals is an extensive quantity, but μ_X is an intensive quantity; therefore, it is useful to rewrite the expression as follows:

$$\mu_X = -k_B T \ln \frac{N}{(N_X + 1)} \left\{ \frac{1}{N \Lambda_X^3} \frac{\int_V d\mathbf{R}_1 \dots d\mathbf{R}_N d\mathbf{R}_{N+1} e^{-U(\mathbf{R}_1, \dots, \mathbf{R}_N, \mathbf{R}_{N+1}; T)/k_B T}}{\int_V d\mathbf{R}_1 \dots d\mathbf{R}_N e^{-U(\mathbf{R}_1, \dots, \mathbf{R}_N; T)/k_B T}} \right\} \quad [53]$$

so that the value in curly brackets is now independent on system size. By setting $c_X = N_X/N$ (which in the limit of large N and N_X is the same as $(N_X + 1)/N$) and

$$\tilde{\mu}_X = -k_B T \ln \left\{ \frac{1}{N \Lambda_X^3} \frac{\int_V d\mathbf{R}_1 \dots d\mathbf{R}_N d\mathbf{R}_{N+1} e^{-U(\mathbf{R}_1, \dots, \mathbf{R}_N, \mathbf{R}_{N+1}; T)/k_B T}}{\int_V d\mathbf{R}_1 \dots d\mathbf{R}_N e^{-U(\mathbf{R}_1, \dots, \mathbf{R}_N; T)/k_B T}} \right\} \quad [54]$$

we can rewrite the chemical potential in our final expression:

$$\mu_X(p, T, c_X) = k_B T \ln c_X + \tilde{\mu}_X(p, T, c_X) \quad [55]$$

The first term of eqn [55] depends only on the number of particles of solute present in the solution, while the second term is also responsible for all possible chemical interactions.

For small concentration of solute, we can make a Taylor expansion of $\tilde{\mu}_X$:

$$\tilde{\mu}_X = \mu_X^0 + \lambda c_X + o(c_X^2) \quad [56]$$

where $\lambda = (\partial \tilde{\mu}_X / \partial c_X)_{p,T}$. If the solution is so dilute that the particles of the solute do not interact with each other, we can stop the expansion to the first term, and we have

$$\mu_X(p, T, c_X) = k_B T \ln c_X + \mu_X^0(p, T) \quad [57]$$

A system in which eqn [57] is strictly satisfied is called an ideal solution.

To find an expression for the chemical potential of the solvent, we employ the Gibbs–Duhem equation, which for a system at constant pressure and constant temperature reads (Wannier, 1966)

$$\sum_i N_i d\mu_i = 0 \quad [58]$$

In particular, in our two-component system, the Gibbs–Duhem equation implies

$$c_A d\mu_A + c_X d\mu_X = 0 \quad [59]$$

which gives (Alfè et al., 2002c)

$$\mu_A(p, T, c_X) = \mu_A^0(p, T) + (k_B T + \lambda_X(p, T)) \ln(1 - c_X) + \lambda_X(p, T) c_X + O(c_X^2) \quad [60]$$

where μ_A^0 is the chemical potential of the pure solvent. To linear order in c_X , this gives

$$\mu_A(p, T, c_X) = \mu_A^0(p, T) - k_B T c_X + O(c_X^2) \quad [61]$$

Despite that μ_A^0 is the chemical potential of the pure solvent, note that μ_X^0 is not the chemical potential of the pure solute, unless the validity of eqn [57] extends all the way up to $c_X = 1$.

2.15.3.3.6 First-principles calculations of chemical potentials

To calculate μ_X , it is useful to consider the difference in chemical potential between the solute and the solvent $\mu_{XA} = \mu_X - \mu_A$, which is equal to the change of Helmholtz free energy of the system as one atom of the solvent is transmuted into an atom of solute at constant volume V and constant temperature p . This transmutation does not obviously correspond to a real physical process, but provides a perfectly rigorous way of calculating the difference of chemical potentials:

$$\mu_{XA} = k_B T \ln \frac{c_X}{1 - c_X} + 3k_B T \ln(\Lambda_X / \Lambda_A) + m(c_X) \quad [62]$$

where Λ_X and Λ_A are the thermal wavelengths of solute and solvent and

$$m(c_X) = -k_B T \ln \frac{\int_V d\mathbf{R} e^{-\beta U(N_A - 1, N_X + 1; \mathbf{R})}}{\int_V d\mathbf{R} e^{-\beta U(N_A, N_X; \mathbf{R})}} \quad [63]$$

with $U(N_A, N_X; \mathbf{R})$ being the potential energy of the system with N_A atoms of solvent and N_X atoms of solute and $U(N_A - 1, N_X + 1; \mathbf{R})$ being the one for the system in which one of the atoms of solvent has been transmuted into the solute.

The thermodynamic integration technique described in Section 2.15.3.3.3 can now be used to compute $m(c_X)$ in the liquid state. This is done by defining an intermediate potential $U_\lambda = \lambda U(N_A - 1, N_X + 1; \mathbf{R}) + (1 - \lambda) U(N_A, N_X; \mathbf{R})$, so that $m(c_X)$ can be expressed as

$$m(c_X) = \int_0^1 d\lambda \langle U(N_A - 1, N_X + 1) - U(N_A, N_X) \rangle_\lambda \quad [64]$$

In practice, the calculation of $m(c_X)$ is done by performing two separate simulations, one with N_A atoms of solvent and N_X atoms of solute and the other with $N_A - 1$ atoms of solvent and $N_X + 1$ atoms of solute. At the end of each time step, forces are computed in both systems, and their linear combination $f_\lambda = \lambda f(N_A - 1, N_X + 1) + (1 - \lambda) f(N_A, N_X)$ is used to evolve the system in time in order to compute the thermal average $\langle U(N_A - 1, N_X + 1) - U(N_A, N_X) \rangle_\lambda$. This is repeated at a number of different values of λ , and the integral is performed numerically. Alternatively, an approach similar to the one described in

eqn [45] is also possible, in which λ is slowly varied from zero to one in the course of the simulation.

To improve statistics, it is useful to transmute many atoms of solvent into solute. In this case, one does not obtain directly μ_{XA} at a chosen concentration, but an integral of this over a range of concentrations. However, by repeating the calculations transmuted a different number of atoms at a time, it is possible to extract information about the value of μ_{XA} in a whole range of concentration, as described in Alfè et al. (2002c). To illustrate the feasibility of these kinds of calculations, in Figure 12, we show the value of the integrand in eqn [64] as function of lambda for an iron–oxygen liquid mixture at a pressure of 370 GPa and a temperature of 7000 K. The error in calculating this integral is of the order of 0.1 eV, which is very small for the purposes of evaluating the partitioning of oxygen between solid iron and liquid iron and the depression of melting point resulting from this partitioning (see the succeeding text). This pressure is somewhat higher than the ICB pressure of 330 GPa. The temperature is also higher than the melting temperature of iron; however, it was argued in Alfè et al. (2002c) that this would not change the chemical potential of O by more than 0.3 eV, which again does not have any effect of the conclusions to be presented in the succeeding text.

In the solid state, thermodynamic integration is not the most appropriate way of calculating the chemical potential difference μ_{XA} . This is clear, because in the zero-temperature limit, at infinite dilution, $m(c_X \rightarrow 0)$ is simply the change in internal energy when one atom in the perfect lattice of solvent is replaced by a solute atom, the impurity system being relaxed to equilibrium. This requires only a static calculation of the type described in Section 2.15.3.1. At finite temperatures in the infinite dilution limit, $m(c_X \rightarrow 0)$ can be obtained from the quasi-harmonic vibrational frequencies of the pure A system and the system containing a single X impurity. If anharmonic effects are significant, as they are in the case of O substituted in hcp Fe (Alfè et al., 2000b), thermodynamic integration can be used to estimate the anharmonic effects. These methods can also be generalized to include the variation of $m(c_X)$ with c_X to linear order in c_X (Alfè et al., 2002c).

The evaluation of $m(c_X)$ only gives access to the difference between the chemical potential of the solute and that of the

solvent. Therefore, in order to obtain μ_X , a preliminary calculation of μ_A is necessary. This can be done on the pure solvent system using the techniques described in Section 2.15.3.3.3.

2.15.3.3.7 Volume of mixing

It is often interesting to study the change of volume of a solution as a function of the concentration of solute. To this end, it is useful to express the volume of the system as the partial derivative of the Gibbs free energy with respect to pressure, taken at constant temperature and number of particles:

$$V = (\partial G / \partial p)_{T, N_X, N_A} \quad [65]$$

If we now add to the system one particle of solvent at constant pressure, the total volume changes by v_A and becomes $V + v_A$. We call v_A the partial molar volume of the solvent. The total Gibbs free energy is $G + \mu_A$, so that according to eqn [65], $v_A = (\partial \mu_A / \partial p)_{T, N_X, N_A} = (\partial \mu_A / \partial p)_{T, c_X}$ where the last equality stems from the fact that μ_A only depends on N_X and N_A through the molar fraction c_X (we assume here that c_X does not change when we add one particle of solvent to the system; this is obviously true if the number of atoms of solvent N_A is already very large.). The partial volume in general depends on c_X , p , and T , but under the assumption of ideality, $v_A = (\partial \mu_A^0 / \partial p)_{T, c_X}$ and it depends only on p and T . In an ideal solution, v_A is the same as in the pure solvent.

Similarly, the partial molar volume of the solute is $v_X = (\partial \mu_X / \partial p)_{T, c_X}$, which becomes independent on c_X under the assumption of ideality. Notice that this is not in general equal to the partial volume of the pure solute.

As an example of the calculation of partial molar volumes, we mention the partial molar volumes of iron and X, with X being either sulfur or silicon or oxygen, obtained by Alfè et al. (2002d) in a binary mixture of iron at the conditions mentioned above of $p = 370$ GPa and $T = 7000$ K. These were $v_{Fe} = 6.97 \text{ \AA}^3$, $v_{Si} = 6.65 \text{ \AA}^3$, $v_S = 6.65 \text{ \AA}^3$, and $v_O = 4.25 \text{ \AA}^3$. Although ideality was not assumed in these calculations, the partial molar volumes of Si, S, and O were found to be rather independent from their concentration in liquid Fe. It is interesting to note that both sulfur and silicon have a partial molar volume that is very similar to that of iron, while oxygen is significantly smaller. This is the main reason of the large difference in the behavior of sulfur and silicon on the one side and oxygen on the other and the resulting partitioning of oxygen between solid and liquid iron (see the succeeding text).

2.15.3.3.8 Solid liquid equilibrium

We want to study now the conditions that determine equilibrium between solid and liquid and in particular how the solute partitions between the two phases and how this partitioning affects the melting properties of the solution. Thermodynamic equilibrium is reached when the Gibbs free energy of the system is at its minimum, and therefore, $0 = dG = d(G^l + G^s)$, where superscripts 's' and 'l' indicate quantities in the solid and the liquid, respectively. In a multicomponent system, the Gibbs free energy can be expressed in terms of the chemical potentials of the species present in the system (Mandl, 1997; Wannier, 1966):

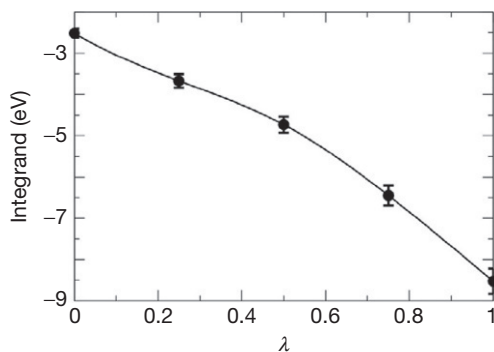


Figure 12 The integrand $\langle U_1 - U_0 \rangle_\lambda$ (eV units) appearing in the thermodynamic integration formula in eqn [64]. Results shown refer to oxygen solute for $N_X = 12$ and $N = 64$. Filled circles show values computed from ab initio m.d. simulations, with bars indicating statistical errors. Curve is a polynomial fit to the computed values.

$$G = \sum_i N_i \mu_i \quad [66]$$

Using eqn [66] and the Gibbs–Duhem equation [58], we obtain

$$dG = \sum_i \mu_i dN_i \quad [67]$$

If the system is isolated, particles can only flow between the solid and the liquid, and we have $dN_i^s = -dN_i^l$, which implies

$$dG = \sum_i dN_i (\mu_i^l - \mu_i^s) \quad [68]$$

If $\mu_i^l < \mu_i^s$, there will be a flow of particles from the solid to the liquid region ($dN_i > 0$), so that the Gibbs free energy of the system is lowered. The opposite will happen if $\mu_i^l > \mu_i^s$. The flow stops at equilibrium, which is therefore reached when $\mu_i^l = \mu_i^s$. In particular, in our two components system, equilibrium between the solid and liquid implies that the chemical potentials of both the solvent and solute are equal in the solid and liquid phases:

$$\begin{aligned} \mu_X^s(p, T_m, c_X^s) &= \mu_X^l(p, T_m, c_X^l) \\ \mu_X^s(p, T_m, c_X^s) &= \mu_A^l(p, T_m, c_X^l) \end{aligned} \quad [69]$$

where T_m is the melting temperature of the solution at pressure p . Using eqn [55], we can rewrite the first of the two equations in the preceding text as

$$\tilde{\mu}_X^s(p, T_m) + k_B T_m \ln c_X^s = \tilde{\mu}_X^l(p, T_m) + k_B T_m \ln c_X^l \quad [70]$$

From which, we obtain an expression for the ratio of concentrations of solute between the solid and the liquid:

$$c_X^s/c_X^l = \exp \left\{ \left[\tilde{\mu}_X^l(p, T_m) - \tilde{\mu}_X^s(p, T_m) \right] / k_B T_m \right\} \quad [71]$$

In general, $\tilde{\mu}_X^l < \tilde{\mu}_X^s$, because the greater mobility of the liquid can usually better accommodate particles of solute, and therefore, their energy (chemical potential) is lower. This means that the concentration of the solute is usually smaller in the solid.

Equation [71] was used by Alfè et al. (2000c, 2002c,d) to put constraints on the composition of the Earth's core. The constraints came from a comparison of the calculated density contrast at inner-core boundary and that obtained from seismology, which is between $4.5 \pm 0.5\%$ (Masters and Shearer, 1990) and $6.7 \pm 1.5\%$ (Masters and Gubbins, 2003). This density contrast is significantly higher than that due to the crystallization of pure iron and therefore must be due to the partitioning of light elements between the solid and liquid. Alfè et al. (2000c, 2002c,d) considered sulfur, silicon, and oxygen as possible impurities and using first principles obtained the partitions for each impurity. The calculations showed that for both sulfur and silicon, $\tilde{\mu}_X^l$ and $\tilde{\mu}_X^s$ are very similar, which means that c_X^s and c_X^l are also very similar, according to eqn [71]. As a result, the density contrast of a Fe/S or a Fe/Si system is not much different from that of pure Fe and still too low when compared with the seismological data. By contrast, for oxygen, $\tilde{\mu}_O^l$ and $\tilde{\mu}_O^s$ are very different, and the partitioning between the solid and liquid is very large. This results in a much too large density contrast, which also does not agree with the seismological data. These results are

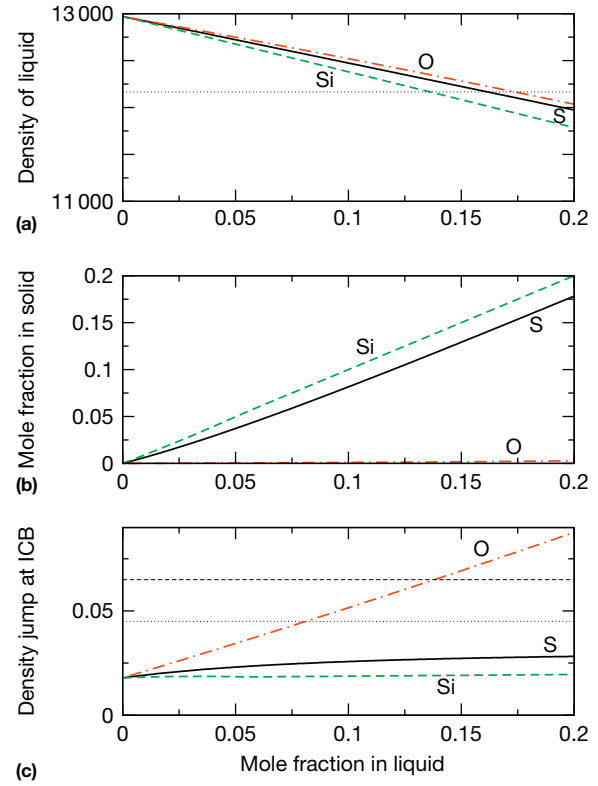


Figure 13 Liquid and solid impurity mole fractions c_X^l and c_X^s of impurities $X = S, Si$, and O and resulting densities of the inner and outer core of the Earth predicted by first-principles simulations. Solid, dashed, and chain curves represent S, Si , and O , respectively. (a) Liquid density ρ^l (kg m⁻³ units); horizontal dotted line shows density from seismic data (Dziewonski and Anderson, 1981; Masters and Shearer, 1990); (b) mole fractions in solid resulting from equality of chemical potentials in the solid and liquid; (c) relative density discontinuity $\delta\rho/\rho^l$ at the ICB; horizontal dotted and dashed lines are values from free oscillation data (Masters and Gubbins, 2003; Masters and Shearer, 1990). Adapted from Alfè D, Gillan MJ, and Price GD (2002) *Earth and Planetary Science Letters* 195: 91, with permission. Copyright 2002 Elsevier.

summarized in Figure 13. The conclusion from these calculations was that none of these binary mixtures can be viable for the core. The density contrast can of course be explained by ternary or quaternary mixtures. Assuming no cross correlated effects between the chemical potentials of different impurities and based on the seismological density contrast of $4.5 \pm 0.5\%$ (Masters and Shearer, 1990), Alfè et al. (2002c,d) proposed an inner core containing about 8.5% of sulfur and/or silicon and almost no oxygen and an outer core containing about 10% of sulfur and/or Si and an additional 8% of oxygen. The more recent seismological datum of $6.7 \pm 1.5\%$ (Masters and Gubbins, 2003) would change the estimate of the core composition to an inner core containing about 7% of sulfur and/or silicon and still almost no oxygen and an outer core containing about 8% of sulfur and/or Si and an additional 13% of oxygen. One consequence of the large partitioning of oxygen between the solid and liquid is that as the solid core grows, it expels oxygen in the liquid, which by converting its gravitational energy helps driving the convective motions that are

responsible for the generation of the Earth's magnetic field (Gubbins et al., 2004).

2.15.3.3.9 Shift of freezing point

The partitioning of the solute between the solid and the liquid is generally responsible for a change in the melting temperature of the mixture with respect to that of the pure solvent. To evaluate this, we expand the chemical potential of the solvent around the melting temperature of the pure system, T_m^0 :

$$\mu_A(p, T_m, c_X) = \mu_A(p, T_m^0, c_X) - s_A^0 \delta T + \dots \quad [72]$$

where $\delta T = (T_m - T_m^0)$ and $s_A^0 = -(\partial \mu_A / \partial T)_{T=T_m^0}$ are the entropy of the pure solvent at T_m^0 . We now impose continuity across the solid/liquid boundary:

$$\mu_A^{0s}(p, T_m^0) - s_A^{0s} \delta T - k_B T_m c_X^s = \mu_A^{0l}(p, T_m^0) - s_A^{0l} \delta T - k_B T_m c_X^l \quad [73]$$

where we have considered only the linear dependence of μ_A on c_X (see eqn [61]). Noting that $\mu_A^{0s}(p, T_m^0) = \mu_A^{0l}(p, T_m^0)$, we have

$$\delta T = \frac{k_B T_m}{s_A^{0l} - s_A^{0s}} (c_X^s - c_X^l) \quad [74]$$

Since usually $c_X^s < c_X^l$, there is generally a depression of the freezing point of the solution.

Using eqn [74] and the composition estimated from the density contrast of 4.5%, Alfè et al. (2002c,d) estimated a depression of about 600–700 K of the melting temperature of the core mixture with respect to the melting temperature of pure Fe, and they suggested an inner-core boundary temperature of about 5700 K. This estimate would go down by a further 300 K if the latest estimate of 6.7% for the density contrast at ICB was used (Masters and Gubbins, 2003), which would therefore result in a temperature at the ICB of about 5500 K.

2.15.3.3.10 Electrical and thermal conductivity

Electrical and thermal conductivities of materials can be calculated from first principles. In particular, in the context of DFT, the frequency-dependent electrical conductivity can be calculated by using the Kubo–Greenwood formula (Kubo, 1957; Greenwood, 1958), which for a particular $\mathbf{k}$ -point in the BZ of the simulation supercell and for a particular configuration of the ions $\{R_I\}$ reads

$$\sigma_{\mathbf{k}}(\omega; R_I) = \frac{2\pi e^2 \hbar^2}{3m^2 \omega \Omega} \sum_{i,j=1}^n \sum_{\alpha=1}^3 [F(\varepsilon_{i,\mathbf{k}}) - F(\varepsilon_{j,\mathbf{k}})] |\langle \Psi_{j,\mathbf{k}} | \nabla_{\alpha} | \Psi_{i,\mathbf{k}} \rangle|^2 \delta(\varepsilon_{j,\mathbf{k}} - \varepsilon_{i,\mathbf{k}} - \hbar\omega) \quad [75]$$

where ω is the angular frequency; e and m are the electron charge and mass, respectively; $\hbar$ is the Planck's constant divided by 2π ; Ω is the volume of the simulation cell; and n is the number of Kohn–Sham states. The α sum runs over the three spatial directions. $\Psi_{i,\mathbf{k}}$ is the Kohn–Sham wave function corresponding to eigenvalue $\varepsilon_{i,\mathbf{k}}$, and $F(\varepsilon_{i,\mathbf{k}})$ is the Fermi weight. The δ function is represented by a Gaussian, with a width chosen to be roughly equal to the average spacing between the eigenvalues weighted by the corresponding change in the Fermi function (Desjarlais et al., 2002). In a liquid or in a solid above zero temperature, the frequency-dependent conductivity is obtained by taking the thermal average:

$$\sigma(\omega) = \left\langle \sum_{\mathbf{k}} \sigma_{\mathbf{k}}(\omega; R_I) W(\mathbf{k}) \right\rangle \quad [76]$$

where $W(\mathbf{k})$ is the weighting factor for the point $\mathbf{k}$. The dc conductivity σ_0 is given by the value of $\sigma(\omega)$ in the limit $\omega \rightarrow 0$.

In a free electron liquid, the electronic part of the thermal conductivity κ_0 and the electrical conductivity σ_0 are related by the Wiedemann–Franz law (Wiedemann and Franz, 1853), $L = \kappa_0 / \sigma_0 T$, where L is the Lorenz number. In a real liquid, the validity of the Wiedemann–Franz law is not necessarily expected, and in fact, a number of exceptions for metals at near-ambient conditions are known (see, e.g., Kittel, 1996). However, the electronic component of the thermal conductivity κ_0 can be directly calculated using the Chester and Thellung (1961) formulation of the Kubo–Greenwood formula, which reads

$$\kappa(\omega) = \frac{1}{e^2 T} \left(L_{22}(\omega) - \frac{L_{12}(\omega)^2}{\sigma(\omega)} \right) \quad [77]$$

and κ_0 is the value of $\kappa(\omega)$ in the limit $\omega \rightarrow 0$. The kinetic coefficients $L_{lm}(\omega)$ are given by Mazevet et al. (2010)

$$L_{lm}(\omega) = (-1)^{(l+m)} \frac{2\pi e^2 \hbar^2}{3m^2 \omega \Omega} \sum_{i,j=1}^n \sum_{\alpha=1}^3 [F(\varepsilon_{i,\mathbf{k}}) - F(\varepsilon_{j,\mathbf{k}})] |\langle \Psi_{j,\mathbf{k}} | \nabla_{\alpha} | \Psi_{i,\mathbf{k}} \rangle|^2 \times [\varepsilon_{j,\mathbf{k}} - \mu]^{(l-1)} [\varepsilon_{i,\mathbf{k}} - \mu]^{(m-1)} \delta(\varepsilon_{j,\mathbf{k}} - \varepsilon_{i,\mathbf{k}} - \hbar\omega) \quad [78]$$

where μ is the chemical potential.

As an example of a recent application, I mention the first-principles calculation of electrical and thermal conductivities of iron and iron alloys (Pozzo et al., 2012, 2013) under the Earth's core conditions, which are displayed in Figure 14. The conductivities have been calculated on three possible adiabatic pressure–temperature profiles, anchored at the ICB temperatures of 6350, 5700, and 5500 K, corresponding to the DFT melting temperatures of pure iron and iron alloyed with sulfur, silicon, and oxygen, as detailed in the previous section. The values for the electrical and thermal conductivities are in the range $1.1\text{--}1.3 \times 10^6 \Omega^{-1} \text{ m}^{-1}$ and $100\text{--}160 \text{ W m}^{-1} \text{ K}^{-1}$, respectively, with the low/high values corresponding to CMB/ICB pressure–temperature conditions.

The Lorenz parameter is roughly constant on all three adiabats, indicating that the Wiedemann–Franz law is valid throughout the core. For pure iron, the Lorenz parameter varies between 2.47×10^{-8} and $2.51 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$, only slightly higher than its ideal value of $2.44 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$, while for the mixtures, it is reduced in the range $2.17\text{--}2.24 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$. These values are in broad agreement with those recently reported by de Koker et al. (2012).

The calculated electrical conductivities are in good agreement with the experimental data for FeSi up to 140 GPa of Matassov (1977) and for Fe_{0.94}O up to 155 GPa of Knittle et al. (1986), who reported values in the range $1.0\text{--}1.2 \times 10^6 \Omega^{-1} \text{ m}^{-1}$. The thermal conductivities are in agreement with recent experimental findings of Hirose et al. (2011) who reported values for the top of the outer core in the range $90\text{--}130 \text{ W m}^{-1} \text{ K}^{-1}$.

These estimates of thermal and electrical conductivity are two to three times higher than those previously used in the geophysical literature (e.g., Nimmo, 2007; Stacey, 2007).

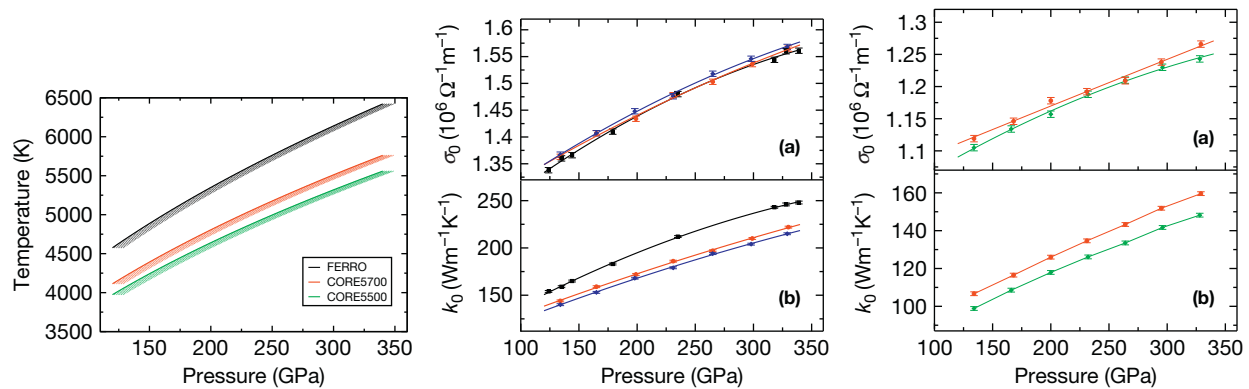


Figure 14 (left) Adiabatic temperature profiles as function of pressure anchored by three possible ICB temperatures T_{ICB} . Black curve (FERRO) corresponds to $T_{\text{ICB}} = 6350$ K, red curve (CORE5700) to $T_{\text{ICB}} = 5700$ K, and green curve to $T_{\text{ICB}} = 5500$ K. Low-pressure edges of the bands (solid line) correspond to the raw DFT–PW91 pressures and high-pressure edges to pressure corrected by 10 GPa, which is the typical DFT–PW91 underestimate of the pressure for iron at core conditions. (center) Electrical (a) and thermal (b) conductivity of liquid iron at the Earth’s core conditions, computed on the FERRO (black), CORE5700 (red), and CORE5500 (blue) adiabats. Lines are quadratic fits to the first-principle raw data (symbols). Error bars (2 SD) are estimated from the scattering of the data obtained from 40 statistical independent configurations. (right) Electrical (a) and thermal (b) conductivities of liquid $\text{Fe}_{0.82}\text{Si}_{0.10}\text{O}_{0.08}$ (red) and liquid $\text{Fe}_{0.79}\text{Si}_{0.08}\text{O}_{0.13}$ (green) mixtures on the CORE5700 and CORE5500 adiabats, respectively. Error bars (2 SD) are estimated from the scattering of the data obtained from 40 statistical independent configurations. Results are obtained with cells including 157 atoms and the single $\mathbf{k}$ -point (1/4, 1/4, and 1/4), which are sufficient to obtain convergence within $< 1\%$. Reproduced from Pozzo M, Davies C, Gubbins D, and Alfè D (2013) *Physical Review B* 87: 014110.

The high thermal conductivity in particular has significant implications for the evolution of the core and the dynamo process generating the Earth’s magnetic field. The convective motions in the outer core that are responsible for the Earth’s dynamo are driven by a combination of thermal and chemical buoyancy sources. The strength of thermal driving is measured by the amount of excess heat that cannot be conducted down the adiabatic gradient; higher thermal conductivity increases adiabatic conduction and therefore decreases the effectiveness of thermal buoyancy relative to chemical buoyancy. Maintaining the same magnetic field with less available thermal buoyancy requires a faster core cooling rate or a higher concentration of radiogenic elements in the core or a combination of the two. Moreover, a faster cooling rate implies that the inner core, which is already thought to be a relatively young feature of the Earth (age ~ 1 Ga; Labrosse et al., 2001), is even younger.

2.15.4 Conclusions

I have described here some ab initio techniques, based on the fundamental laws of quantum mechanics, that are currently being used to study the properties of high-pressure and high-temperature minerals. I have focused our discussion to the formulation of quantum mechanics known as DFT, with various approximations for the XC functional, and I have shown that this technique can predict very reliably a number of static and elastic properties, like low-temperature equation of states, phase transition, and elastic constants. DFT has also been successfully used to predict the vibrational properties of a large number of materials, and the examples provided here show that these predictions are in good agreement with the experimental data, at both zero pressure and high pressure. To study the high-temperature properties of solids and liquids, ab initio techniques

coupled with MD have been proven to be a powerful and reliable tool for both solids and liquids. I have illustrated this mentioning the calculation of the high-temperature elastic constants of the mantle-forming minerals MgSiO_3 in both the perovskite and the recently discovered postperovskite phases and the elastic behavior of hcp iron under the conditions of the Earth’s inner core and the dynamic properties of liquids like diffusion and viscosity.

A major contribution to the calculation of the ab initio high-pressure and high-temperature properties of minerals has been given by the possibility of calculating free energies, and I have described how this can be done for both liquids and solids, using the technique of thermodynamic integration. The access to the free energies of materials has allowed the calculation of a number of thermodynamic properties. Here, I have described the calculation of melting properties and in particular the melting curve of iron under Earth’s core conditions. I have also shown how ab initio techniques coupled with thermodynamic integration can be used to calculate chemical potentials in binary solutions and illustrated the method by showing the calculation of the chemical potentials of oxygen, sulfur, and silicon in solid and liquid iron at the Earth’s core conditions. These calculations were used in conjunction with seismological data to estimate the probable composition of the Earth’s inner and outer core. I have also shown that it has become possible to compute transport properties like the electrical and thermal conductivities, and I have mentioned recent calculations applied to the Earth’s core.

In our description of melting properties, I have pointed out that current XC functionals do not always provide perfect agreement with the experiments. I have shown how the application of empirical corrections can improve these results, but this is not a completely satisfactory solution, as it introduces some arbitrariness in the calculations, which do not conform to our original definition of ab initio anymore. Therefore, it is

important to be able to go beyond DFT, and for this, I have mentioned QMC techniques, which I believe are sufficiently accurate and general that they will become a major player in the field of first-principles calculations of material properties. The development of these techniques will be helped by the availability of ever more powerful computers.

I have also mentioned the technique of the coexistence of phases to calculate melting curves. This technique is intrinsically very expensive, as it needs calculations performed on systems containing hundreds or even thousands of atoms. However, recently, it has just become possible to apply this technique in the context of ab initio calculations, with simulations reported on up to 1728 atom cells. I have illustrated this method with the recent calculation of the melting curve of MgO under the Earth's mantle conditions. The availability of faster computers will help make this coexistence calculations more routinely applied and possibly will also allow simulation of the eutectic behavior of solutions, in which a liquid is in coexistence with more than one solid phase.

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2.16 Dynamic Compression

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2.16.1 Dynamic Compression Versus Static Compression

Experimental techniques in high-pressure geophysics can be usefully classified by the strain rate or timescale involved in the measurement. At the longest timescales or slowest strain rates lie static high-pressure methods, in which forces applied to samples are fully supported by opposing forces. In such experiments, stresses are approximately hydrostatic and constant in time, strain rates are approximately zero, and the duration of an experiment is set by criteria like achievement of equilibrium, stability of the pressure vessel, availability of experimental resources, or the patience of the experimentalist. Static methods include cold seal (Jacobs and Kerrick, 1980)

and internally heated pressure vessels (Holloway et al., 1992), piston-cylinder devices (Boyd and England, 1960), opposed anvil and multianvil devices (Kawai and Endo, 1970), and diamond anvil cells (Mao et al., 1978; Merrill and Bassett, 1974). In many of these assemblies, the experimentalist has direct control and measurement of experimental temperature and ability to control applied load and to infer pressure according to some calibrated pressure scale; only the relatively low-pressure (up to about 0.5 GPa) gas–medium-pressure vessels allow absolute pressure measurement. These methods are suitable for phase equilibrium and partitioning studies, elastic constant measurements, crystal structure determinations, and more. Next, there are quasistatic methods, in which accelerations are negligible, but forces are not quite hydrostatic or not

quite balanced within the apparatus, allowing steady sample deformation to be observed at strain rates up to $\sim 10^{-2} \text{ s}^{-1}$. In such cases, experimental duration is determined mostly by the maximum accumulated strain necessary to observe a certain texture or allowed by the apparatus. Quasistatic methods include Paterson (1970) and Griggs (Tingle et al., 1993) apparatuses, split cylinder compression, rotating Drickamer cells, and D-DIA-type multianvil devices. It remains possible to control experimental temperature at a prescribed value. At higher strain rates, we move into the dynamic compression domain. The quasi-isentropic compression and rapid deformation method regime encompasses strain rates up to $\sim 10^6 \text{ s}^{-1}$. Methods include magnetically driven ramp compression (Ding and Asay, 2007), graded density impacts (Nguyen et al., 2006), and split Hopkinson bars (Davies and Hunter, 1963). In this domain, temperature becomes a dependent variable, as there is insufficient time for conduction of heat through sample and apparatus to maintain equilibrium with an external heat bath. Instead, the assumption of adiabatic changes in state becomes a more accurate way to define the energy budget. Sample stresses become dynamic, time-variable quantities, typically not controlled directly but rather determined by conservation of momentum as impulses are transmitted to a sample. Finally, at the highest strain rates (exceeding 10^9 s^{-1}) lie shock compression methods, including elastic shocks at low stresses and plastic shocks at higher stresses. Shocks can meaningfully be approximated as instantaneous step changes in stress, density, internal energy, temperature, and particle velocity. Stable compression shocks are adiabatic but not reversible, with the entropy of the compressed state necessarily being higher than the uncompressed state. Temperature and pressure behind the shock can be measured or inferred from conservation equations, but they are not independently controllable except through manipulation of the initial state of the sample.

2.16.1.1 Impact Studies: Cratering, Failure, and Flow

Impact phenomena at scales ranging from micrometeoroids to catastrophic planetary collisions are important in understanding the solar system, encompassing issues from the initial accretion of planets to the shaping of their modern surfaces. Attempts to understand impact phenomena are a clear application of experimental shock compression studies, in two distinct ways. The first directly examines the three-dimensional (3D) geometry and time evolution of laboratory-scale craters. The second measures material properties necessary to correctly model the impact process in hydrodynamic simulations, including equations of state and material failure criteria. Impact studies, however, are not the primary focus of this chapter; the reader is directed to a comprehensive recent book (Osinski and Pierazzo, 2012).

2.16.1.2 Material Properties

The relevance of shock compression to impact phenomena is immediately clear, but understanding of many geophysical and planetary problems that do not involve impacts or high strain rates nevertheless can be informed by dynamic compression experiments. Essentially, this is because dynamic compression experiments yield an absolute pressure scale and allow

determination of numerous material properties that are relevant to static natural situations yet are difficult to measure in static experiments. This type of research is the focus of this chapter on geophysics and dynamic compression. A number of comprehensive review articles and books on this subject have been published that summarized the state of the field at the time (McQueen, 1968, 1989; McQueen et al., 1970) and many of the developments can be best followed through the regularly published proceedings of the biannual Shock Compression of Condensed Matter conferences.

Dynamic compression experiments mostly explore one of the three families of state points: the Hugoniot, the quasi-isentrope, and the release isentrope. The meaning of these terms (as well as the familiar isotherm) is shown in Figure 1 for the simple, analytic case of a monatomic ideal gas. The behavior of each family of state points in real materials is discussed in more detail in the succeeding text.

2.16.1.2.1 The Hugoniot

Consider a material at some initial uncompressed state, with given composition, phase (or phase assemblage), bulk density, internal energy, entropy, and temperature. When a shock front passes through the material, its state changes rapidly along a path called a Rayleigh line to a final compressed state with the same bulk composition but some possibly transformed phase assemblage, higher than initial bulk density, internal energy, entropy, and temperature (Figure 2). Conservation of momentum applied to each infinitesimal layer of a steady propagating shock shows that the Rayleigh line really is a line in the pressure–volume plane. The slope of this line is given by the mass flux through the shock front. However, points along the Rayleigh line are not, in general, equilibrium states of the material; that is, they do not plot on the surface given by the relaxed equation of state (EOS) $P = P(V, T)$ for the material in question. To form a stable, steady shock, the Rayleigh line must intersect the EOS at some equilibrium condition, which is then a final shocked state that can persist for some time. A Rayleigh line with a given slope (mass flux) will reach such a state at a unique final point (if the Rayleigh line actually intersects the EOS at more than point, a multiple-wave structure can result). Such a point constitutes one state among a related family of states called the Hugoniot. The locus of all such points that can be reached as shocks with a range of mass fluxes are driven into material at the same initial state traces out the Hugoniot. It is important to understand that the Hugoniot is not the thermodynamic path followed by a material during shock compression; it is instead the family of stable endpoints of Rayleigh line paths of different slope. Typically, supported shock experiments such as those generated by plate impact experiments sample a single point on the Hugoniot in each experiment. On the other hand, decaying shock experiments such as those generated by laser-driven compression may continuously sample a wide range of Hugoniot states in a single experiment.

The term principal Hugoniot is reserved for the Hugoniot that begins from the standard state of a material at 1 bar pressure, $\sim 298 \text{ K}$, and zero porosity and in the stable phase of the material under such conditions. By manipulation of these initial conditions, it is possible for single-shock experiments to explore states both below and above the principal Hugoniot. Preheating of samples and porous materials

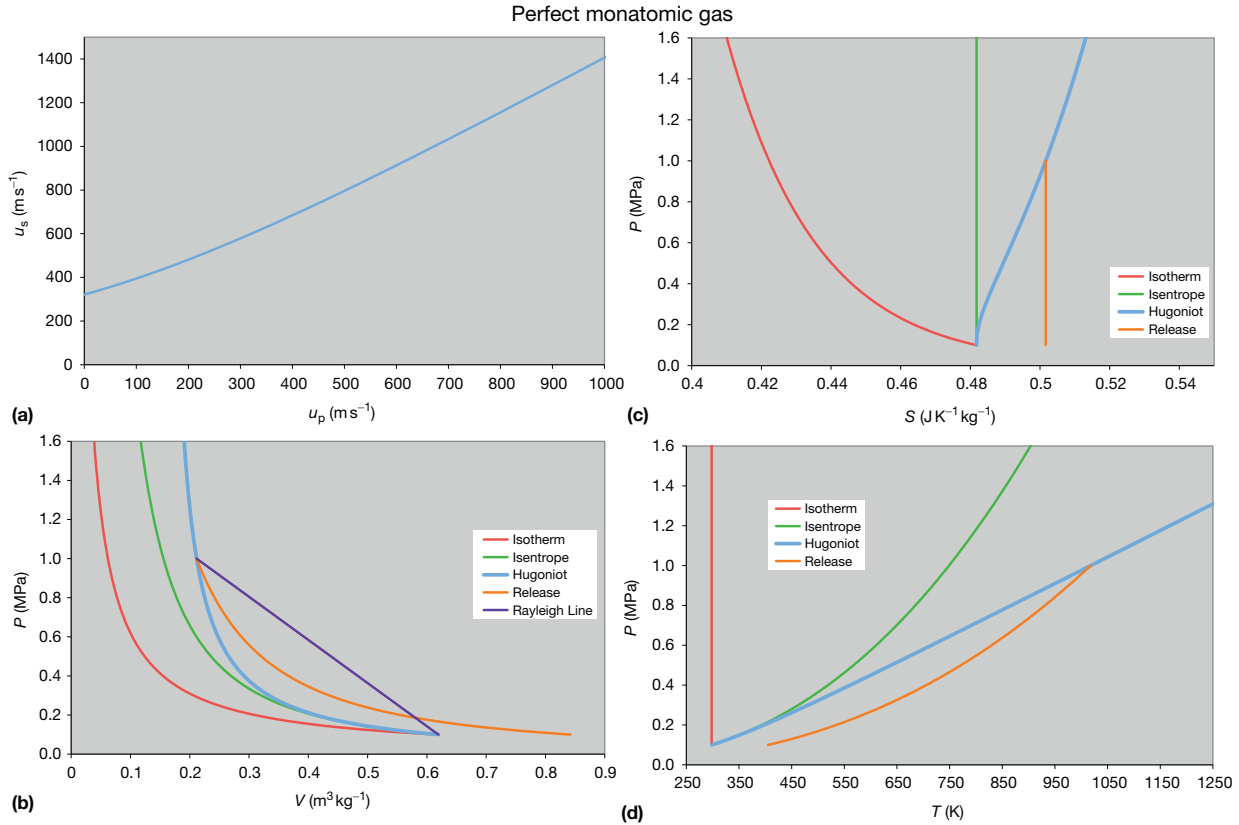


Figure 1 Various thermodynamic paths and special curves illustrated using the analytic equation of state of a monatomic ideal gas of atomic weight 40. (a) The Hugoniot, in the shock velocity (U_s)–particle velocity (u_p) plane. Each point on the curve represents the characteristics of a shock state that can be achieved in a single jump from the standard initial point of 1 bar pressure (P), 298.15 K temperature (T). The intercept at $u_p = 0$ is the sound speed in the gas at ambient conditions, 321.3 m s⁻¹; stronger shocks propagate faster and accelerate gas behind the shock front to increasing particle velocities. In the case of an ideal gas, the Hugoniot is clearly curved at low u_p but approaches a constant slope given by $(\Gamma + 1)/(\Gamma - 1) = 4$, where Γ is the ratio of specific heats (5/3 for a monatomic ideal gas). Note that condensed materials (liquids and solids) more typically show a linear Hugoniot even for weak shocks (as long as they overcome the Hugoniot elastic limit). (b) The P – V plane (V is specific volume, the reciprocal of density). The five curves shown include three thermodynamic paths that can be accomplished by reversible compression, as they lie entirely on the equilibrium equation of state of the gas: the principal isotherm (constant T , red), the principal isentrope (constant entropy S , green), and the release isentrope from a shock state (constant S but higher than that of the principal isentrope, orange). Also shown is the Hugoniot (cyan), a family of equilibrium state points but not one that can be achieved by reversible compression, and an example of a Rayleigh line (purple), representing the actual family of (disequilibrium) states through which material passes during shock compression from ambient conditions to a final shocked state at 1 MPa pressure. (c) The P – S plane, showing the isotherm, isentrope, Hugoniot, and release isentrope as in (b). The entropy decreases along the isotherm ($(\partial S/\partial P)_T$ is generally negative), remains constant along the principal and release isentropes, but increases along the Hugoniot (a necessary criterion for forming stable shocks). (d) The P – T plane, showing the same four families of states as part (c). Here, T is constant along the isotherm (by definition), increases up both the isentrope and (more steeply) along the Hugoniot, and decreases down the release isentrope but reaches a postshock temperature higher than the initial T due to irreversible work done by the shock compression. Finally, note that in (b), (c), and (d), it can be seen that the Hugoniot and the isentrope have the same slope at $P = 1$ bar, and Taylor expansions of these curves differ only in higher-order derivatives.

explores compressed states with energy or temperature states higher than the principal Hugoniot state at given volume, whereas precompression or dense metastable polymorphs explore lower energy or temperature states than those along the principal Hugoniot. Multiple shock or shock-and-partial-release experiments also reach states different from those along the principal Hugoniot.

2.16.1.2.2 The quasi-isentrope

A range of experimental configurations are available for compressing material quickly but without forming a shock. If such compression is rapid enough that heat flow remains negligible

but slow enough to avoid forming a shock, then this path may approach an isentropic compression. Being a spontaneous thermodynamic process, such compression can never truly be isentropic, but in principle, it can be nearly so; hence, this type of experiment is dubbed ‘quasi-isentropic compression.’ To achieve quasi-isentropic conditions generally requires careful control of the loading path and short propagation distances, since ramp compression waves tend to steepen into shocks (Swift et al., 2008). The quasi-isentrope is a useful measurement because it reaches compressed states far below the principal Hugoniot (see Figure 1) that are often directly relevant to planetary interiors (where convection tends to establish nearly

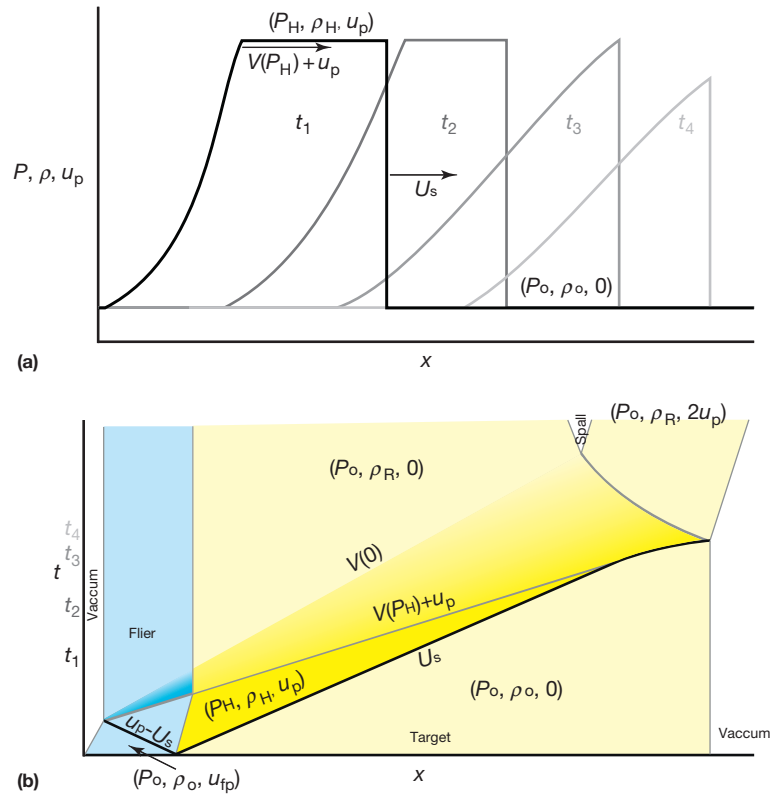


Figure 2 Schematic representation of the evolution of an experimental shock wave. (a) A supported or steady shock, typical of plate impact experiments, is represented in the laboratory reference frame at four different times. The x -coordinate is distance along the shock propagation direction. The curves plotted can represent pressure (P), density (ρ), or particle velocity (u_p) – all three quantities jump from initial, preshock values ($P=P_0 \sim 0$, $\rho=\rho_0$, $u_p=0$) to larger values as the shock front passes. At times t_1 and t_2 , these parameters remain at elevated steady values for the duration of the supported shock and then decrease as the release wave arrives. The shock wave propagates to the right at velocity U_s , whereas the leading edge of the release wave propagates in the laboratory reference frame at the faster velocity $V(P_H)+u_p$, where $V(P_H)$ is the sound speed in the shock-compressed state and may be a longitudinal wave speed or a bulk wave speed depending on whether the material is solid or not. At later time t_3 , the leading edge of the release wave overtakes the shock front and begins to attenuate the shock such that at this time and after the shock wave is nonsteady and the evolution of states at the intersection of the shock front and the leading edge of the release wave trace out a decaying family of points along the Hugoniot. Experiments such as laser-driven and explosive-in-contact shocks that generate decaying shocks from the beginning can be thought of as starting at a time like t_3 . (b) The same shock-and-release experiment is shown in the time–distance plane; the x -scale is the same as in part (a) and times t_1 – t_4 are indicated. Blue colors represent the flier plate, yellow colors represent the target material, and white is vacuum. The density of shading is proportional to material density. Shock waves are shown as heavy black lines. Leading edges of release waves are shown as heavy gray lines. Material interfaces and surfaces are shown as fine gray lines. The impact occurs at $t=0$, launching a shock wave forward into target that accelerates it from rest to u_p and another shock wave backward into flier that decelerates it from u_{fp} to u_p . When the backward propagating shock reaches the rear surface of the flier, it reflects as a release wave that begins a ramp that brings material back to ambient pressure and approximately zero particle velocity. The leading edge of this release wave overtakes the forwards-propagating shock wave at t_3 , after which the shock velocity can be seen slowing down until the attenuated shock reaches the downrange surface of the target at t_4 . The free surface takes off at $\sim 2u_p$ and another release wave propagates back into the target; when the two release waves meet, the stress becomes tensile and a spall is likely to occur.

isentropic pressure–temperature gradients). The determination of material properties using quasi-isentropic compression was reviewed by [Ding and Asay \(2007\)](#). By analogy to the principal Hugoniot, we may distinguish the principal quasi-isentrope that begins from 1 bar pressure, ~ 298 K, and the stable, non-porous phase of a material. Quasi-isentropes anchored at other initial conditions can be measured as well.

2.16.1.2.3 The release isentrope and postshock states

Materials that are shocked to high pressure in the laboratory cannot remain at high pressure indefinitely. Surrounded by the low-pressure laboratory environment, they are released by waves propagating inward from free surfaces. Such release

waves are not shocks (the formation of a decompression shock is rarely stable), but rather, they are ordinary acoustic waves, and hence, they accomplish adiabatic and nearly reversible changes of state. By the second law of thermodynamics, this implies that ‘release isentrope’ is a reasonable approximation to the path of such releases ([Figure 1](#)). These are useful in a number of ways.

The leading edge of a release wave travels into material in the shock state at the speed of sound in the high-pressure material ([Figure 2](#)). In a solid phase, this is a longitudinal or P -wave velocity, whereas in a liquid or vapor phase, it is a bulk sound velocity. The difference between longitudinal and bulk sound speed release waves can be used to determine whether

the material in the shock state is molten or not. The measured sound speeds in minerals at high pressure are of direct interest in the study of elasticity and seismology and constrain a higher-order derivative of the EOS than direct Hugoniot data do. Furthermore, when a bulk sound speed can be observed, the difference between the P - V slope of the Hugoniot and the P - V slope of the release isentrope directly constrains the Grüneisen parameter (e.g., Brown et al., 1987), which is needed among other reasons for thermal pressure corrections to apply Hugoniot EOS measurements at the conditions of planetary interiors. The velocity of release waves is most often determined using methods that locate the overtaking and attenuation of a shock wave by a following release wave. Such overtaking can be observed using velocimetry (see methods in the succeeding text), pyrometry (in transparent samples or in transparent analyzer materials behind opaque samples), or other diagnostics.

The sound speed in the shock state is related to infinitesimal displacements from the Hugoniot state. On the other hand, determination of release states at finite pressure drops, extending in some cases down to zero pressure, also provides important information. For simple compression and release without phase changes, collapse of porosity, or elastic/plastic effects, the difference between the initial and released states constrains the irreversible work done upon compression. In other cases, clear differences between shock-and-release paths can diagnose the presence of important complexities such as phase transitions including melting and vaporization upon release (e.g., Luo et al., 2003). In general, observations of naturally shocked samples – including impact craters on planetary surfaces, materials derived from terrestrial impact events, and meteorites – are in fact analyses of shocked and subsequently released materials in their final, released state. Hence, the study of release paths, postshock amorphization, spallation, and so on is an essential aspect of the interpretation of these samples and their use to constrain preimpact states and the characteristics of the impacts themselves.

2.16.1.3 Important Equations

2.16.1.3.1 Rankine–Hugoniot conservation equations

The fundamental basis for interpreting shock compression experiments is expressed by conservation of mass, momentum, and energy, recast as jump conditions across a shock front in the form of the three Rankine–Hugoniot equations. We will not provide a full derivation here, only a qualitative motivation and interpretation of each; a definitive treatment can be found in Zel'dovich and Raizer (2002). Throughout this chapter, some expressions are most conveniently written using density ρ and others using the reciprocal of density, specific volume V .

First, conservation of mass requires that, in the frame of reference of the shock front, the mass flux (mass per unit time per unit area) entering the shock equals that exiting the shock. This constraint is expressed as

$$\rho_o U_s = \rho (U_s - u_p) \quad [1]$$

where the left-hand side is the mass flux overtaken by the shock front moving at shock velocity U_s into stationary material with initial density ρ_o and the right-hand side is the mass flux out of

the shock front, where material has been compressed to density ρ and is moving at particle velocity u_p in the laboratory reference frame or $(U_s - u_p)$ relative to the shock front.

Second, conservation of momentum requires that the normal stress difference across the shock front is balanced by the impulse delivered to material per unit time. If we assume hydrostatic states of stress both before and after shock passage, such that pressure P may be substituted for normal stress, then this condition is expressed as

$$(P - P_o) = \rho_o U_s u_p \quad [2]$$

where the right-hand side is the mass flux times the velocity to which that mass is accelerated.

Third, conservation of energy can be expressed in a particularly compact form because the passage of a shock is an adiabatic change of state. Hence, the energy change across the shock is given by the work done on the material during compression. Since the change in kinetic energy is known from eqns [1] and [2], the rest of the work goes into increasing the internal energy E :

$$E - E_o = \frac{1}{2}(P + P_o)(V - V_o) \quad [3]$$

The Rankine–Hugoniot jump equations contain the essence of the usefulness of shock compression experiments for EOS studies. The goal in such studies is to determine the function that describes the array of equilibrium states of a material, which is in general a surface in three dimensions or a function of two variables such as $P(V, T)$ or $P(V, E)$. In static experiments, typically, T is imposed, P is determined using a calibrated standard, and V is measured by a method such as x-ray diffraction. In a shock compression experiment, when three variables such as V_o , U_s , and u_p are measured (E_o and P_o are also known), the Rankine–Hugoniot equations provide a solution for P , V , and E . Thus, specific volume (the reciprocal of density) is determined directly from conservation of mass, which works equally well for crystals, liquids, and gases (note that the latter two materials do not provide Bragg diffraction of x-rays necessary to determine molar volume by diffraction). Furthermore, P is determined absolutely, from conservation of momentum, and (at least in a symmetrical experiment where target and projectile are made of the same material) is not referenced to any calibration standard. A large database of symmetrical experiments on metal standards has been available for many years (Walsh et al., 1957) and continues to be extended and improved (Asimow et al., 2009; Mitchell and Nellis, 1981; Nellis et al., 2003), which allows the use of these standards as flier and driver materials in asymmetrical experiments on geologic samples through the impedance matching method (see in the succeeding text). Indeed, many of the calibrated standards used in static experiments have had their equations of state determined by shock wave experiments (Holmes et al., 1989; Jamieson et al., 1982). Finally, the knowledge of internal energy in the shock state provides the basis for determining a number of thermodynamic quantities such as the Grüneisen parameter (see in the succeeding text) or, if temperature is also measured, the heat capacity.

For the determination of the shock compression experimental variables U_s and u_p , there are numerous experimental diagnostics discussed in the succeeding text, but here, we

mention an additional important set of constraints whereby u_p can be determined from, for example, the velocity of a projectile at the moment of impact rather than from direct velocimetry on the shocked material. This is the method of *impedance matching*, which arises from the assumption that, after impact, the conditions for continuity at an interface between two different materials (such as the flier and the driver in a gun experiment) require equality of particle velocity (u_p) and of normal stress (or, for hydrostatic conditions, of pressure P) across the interface. A mismatch in particle velocity implies that the interface is either separating or overlapping in space, and a mismatch of normal stress implies that the interface is accelerating and the full shock front has not yet passed through the interface. The principle of impedance matching is illustrated in Figure 3.

2.16.1.3.2 Equations of state

An 'equation of state' is a functional relationship that closes the description of the physical and thermodynamic properties of a phase by expressing one dependent intensive parameter as a function of two independent intensive parameters. For example, the EOS may give specific volume as a function of pressure and temperature, $V(P,T)$, or conversely, it might be expressed as pressure as a function of volume and temperature, $P(V,T)$. In some cases, internal energy, entropy, or another thermal parameter takes the place of temperature. In geophysics, it is necessary to have the EOS of materials such as minerals, liquids, and gases in order to compute buoyancy, elastic properties, and thermodynamic states at elevated pressure (Chapter 2.08).

Numerous formalisms are available for describing the EOS of geologic materials. These include tabular forms,

polynomials or other easily fitted and manipulated expressions, and empirically or theoretically motivated forms that express the expected behavior of materials under applied stress. The choice of an appropriate form for the EOS is essential for most applications, but this may involve a compromise between rigor and ease of use. A well-chosen functional form should be able to fit available data with a minimum number of free parameters, in order to ensure that parameters are well defined and that the EOS can be used both for interpolation and, as much as possible, for extrapolation.

Since shock compression data determine the EOS of studied materials, it is appropriate to review here some of the commonly used EOS forms to which shock data are fitted.

The natural space in which to express shock compression data is in terms of the parameters that are actually measured in shock experiments: shock velocity U_s and particle velocity u_p . Empirically, it is found that – in the absence of phase transitions, elastic/plastic transitions, initial porosity, or other complications – most condensed materials yield a straight-line relationship between these variables:

$$U_s = C_0 + s u_p \quad [4]$$

where the intercept C_0 is the velocity of an infinitely weak plastic shock and hence should be the zero-pressure bulk sound speed of the material (but note that the $U_s - u_p$ Hugoniot of the ideal gas is not a straight line; see Figure 1). Together with initial volume at reference pressure and temperature, V_0 , eqn [1] defines the family of equilibrium states of a material along the Hugoniot. The Rankine-Hugoniot eqns [1]–[3] in the preceding text allow the relationship [4] to be transformed into curves in the pressure-particle velocity,

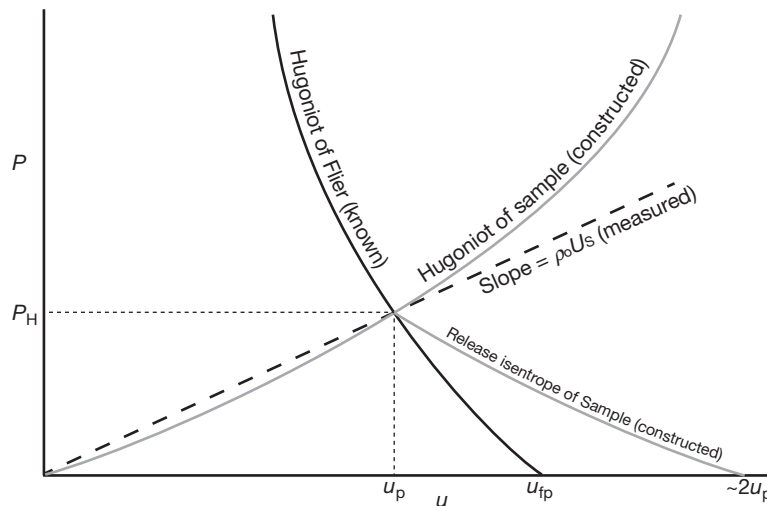


Figure 3 The use of impedance matching to determine pressure (P) and particle velocity (u_p) by imposing continuity at material interfaces. In this experiment, a flier plate – constructed from a standard material whose Hugoniot properties ρ_{0f} , C_{0f} , and s_f are known – is initially moving at velocity u_{fp} (in the laboratory reference frame) and impacts a stationary target material whose Hugoniot is initially unknown. Possible shock states of the flier lie along the black curve $P = \rho_{0f}[C_{0f} + s_f(u_{fp} - u_p)](u_{fp} - u_p)$, from eqns [2] and [4]. The velocity U_s of the resulting shock in the sample is measured, which by eqn [2] implies that the shock state in the sample lies along black dashed line $P = \rho_0 U_s u_p$. Then, the requirement that P and u are continuous across the flier-sample interface locates the shock state at the intersection point (P_H, u_p) . This yields one point on the unknown Hugoniot shown by the heavy gray line, which can be constructed from a series of experiments of this type with different projectile velocities or flier materials. Also shown is a typical release isentrope for the sample, which is often close to a reflection of the Hugoniot, can be measured at multiple points using low-impedance buffers and ends at the free-surface velocity $\sim 2u_p$ at $P = 0$.

pressure–density, pressure–volume, or pressure–energy planes or indeed into a curve in the 3D pressure–volume–energy space. We note that this three-parameter expression can be extended by the addition of higher-order terms (e.g., a quadratic term proportional to u_p^2) if necessary. In order to describe states of a material that do not lie along the principal Hugoniot, eqn [4] must be combined with another expression, such as the Mie–Grüneisen thermal pressure formalism (see in the succeeding text), that extends the Hugoniot curve into a surface in pressure–density–energy or an equivalent 3D phase space. An EOS expressed this way, primarily in $U_s - u_p$ space, is termed a shock wave EOS.

For applications beyond shock compression, moreover, it is more convenient and natural to work with variables such as pressure and volume directly. The most common expressions for cold compression of geologic materials include the Birch–Murnaghan and Vinet EOS, which can be used in their isothermal or isentropic forms. The Birch–Murnaghan isentrope results from a Taylor series expansion in powers of strain and is given by

$$\begin{aligned} P_s &= 3K_{os}f(1+2f)^{5/2}(1+a_3f+a_4f^2\cdots) \\ a_3 &= \frac{3}{2}(K'_s - 4) \\ a_4 &= \frac{3}{2}\left(K''_s K_{os} + K'_s(K'_s - 7) + \frac{143}{9}\right) \end{aligned} \quad [5]$$

where f is the Eulerian strain parameter

$$f = \frac{1}{2} \left(\left(\frac{V_0}{V} \right)^{2/3} - 1 \right) \quad [6]$$

P_s refers to pressure along the principal isentrope at volume V , K_{os} is the isentropic bulk modulus at zero pressure, K'_s is the isentropic pressure derivative of the isentropic bulk modulus also at zero pressure, and K''_s (when needed) is the isentropic second pressure derivative of the isentropic bulk modulus at zero pressure. Most commonly, the Birch–Murnaghan equation is used as in its third-order form (such that $a_4 = 0$); orders beyond fourth are very rarely used. The Birch–Murnaghan equation can also be used to express an isotherm simply by replacing K_{os} with K_{oT} and K'_s with K'_T . The isothermal Vinet EOS is given by

$$\begin{aligned} P &= 3K_{oT}x^{-2}(1-x)e^{\eta(1-x)} \\ \eta &= \frac{3}{2}(K'_T - 1); \quad x = \left(\frac{V}{V_0} \right)^{1/3} \end{aligned} \quad [7]$$

There are numerous other EOS formalisms, some in common use. A comprehensive discussion of the relationships between various finite strain and shock wave EOS formalisms is provided by Jeanloz (1989). In the limit of zero strain, the intercept C_o of the linear $U_s - u_p$ shock wave EOS is expected to be equal to the bulk sound speed, $(V_o K_{os})^{1/2}$, and the slope s should be related to the pressure derivative of the bulk modulus by $K'_s = 4s - 1$; these relationships are simple consequences of equating corresponding terms in the finite strain and particle velocity power series (Jeanloz and Grover, 1988; McQueen et al., 1970; Ruoff, 1967).

2.16.1.3.3 Mie–Grüneisen approximation and Grüneisen parameters

The thermodynamic Grüneisen parameter, also called the Grüneisen gamma or first Grüneisen parameter, expresses thermal pressure at constant volume and can be related by various thermodynamic identities to other derivative material properties:

$$\gamma = V \left(\frac{\partial P}{\partial E} \right)_V = \frac{V}{C_V} \left(\frac{\partial P}{\partial T} \right)_V = \frac{V\alpha K_T}{C_V} = - \left(\frac{\partial \ln T}{\partial \ln V} \right)_S \quad [8]$$

where C_V is isochoric heat capacity, α is isobaric thermal expansion coefficient, and subscript S in the last partial derivative refers to constant entropy. One major reason why γ is a convenient parameter to express thermal pressure is that for many materials, it is found that γ is well approximated as a single-parameter function of V only, whereas in general, most thermodynamic derivatives are function of two parameters. Taking $\gamma = \gamma(V)$ is equivalent to the Mie–Grüneisen approximation, and it allows integrals at constant volume to be replaced with finite difference expressions. For example, if the internal energies of corresponding points on the isentrope (E_s) and on the Hugoniot (E_H) are known at equal volume V , we may derive the pressure on the Hugoniot (P_H) from the isentropic EOS ($P_s(V)$) and the Mie–Grüneisen approximation:

$$P_H(V) - P_s(V) = \frac{\gamma(V)}{V} [E_H(V) - E_s(V)] \quad [9]$$

where $E_H(V)$ is known from eqn [3] and $E_s(V)$ can be obtained by integrating, for example, eqn [5], since from elementary thermodynamics $(\partial E / \partial V)_S = -P$. It remains to choose a functional form to express the variation of γ with volume. A convenient expression that has found wide use in shock wave work is

$$\gamma(V) = \gamma_o \left(\frac{V}{V_o} \right)^q \quad [10]$$

where $q \sim 1$ for many solids and q may be negative for silicate liquids (Asimow and Ahrens, 2010; Brown et al., 1987; Mosenfelder et al., 2007, 2009; Stixrude and Karki, 2005; Stixrude et al., 2009). Other forms, however, are frequently adopted by various authors, motivated by better description of data or computations or by various theoretical limits such as $\gamma = 2/3$ in the Thomas–Fermi limit at very high compression (Gilvarry, 1957).

To relate states at specified internal energy to states at specified temperature, it is necessary to specify the heat capacity of the material. In many cases, the isobaric heat capacity C_P is measured at ambient pressure, but it may be transformed to the isochoric heat capacity C_V using

$$\frac{C_P}{C_V} = 1 + \alpha \gamma T \quad [11]$$

Various theoretical forms are available for C_V as well; the Debye formalism is often adequate, especially at high temperature. Given models of the volume dependence of γ and the volume and temperature dependence of C_V , the shock temperature as a function of volume can be predicted by adding the temperature increase along the isentrope to the temperature increase along the isochore between isentrope and Hugoniot. For the case where C_V is treated as constant at a given volume:

$$T_H = T_o \int_{V_o}^V \frac{-\gamma(V)}{V} dV + \frac{\gamma(V)}{VC_V(V)} [E_H(V) - E_S(V)] \quad [12]$$

whereas if C_V varies with T , an implicit expression is required.

2.16.2 Experimental Methods

A discussion of experimental methods for shock compression research naturally divides into loading methods, that is, options for driving or generating a rapid high-pressure event; diagnostic methods, that is, options for measuring the response of target materials during or after the event; and interpretive methods, that is, data processing, modeling, or computational strategies to determine desired material properties from raw measurements.

2.16.2.1 Dynamic Loading Methods

The first requirement for experimental study of dynamic compression is an apparatus for dynamically compressing materials of interest in a safe, controlled manner. A number of technologies are available for doing so; these are discussed in turn here.

2.16.2.1.1 Guns

A gun is any device for accelerating a projectile in a particular direction that features a barrel or rail to guide the projectile toward a target as it accelerates. Projectiles may be accelerated by detonation of propellants, release of compressed gases, or electromagnetic forces. The performance of a given gun system can be expressed in terms of the range of usable projectile masses; the range and reproducibility of projectile velocities achievable; and quality issues such as tilt, planarity, and targeting accuracy.

For low velocities, up to a few hundred meters per second, a pulse of compressed gas released uprange of a projectile provides sufficient acceleration. In the range from hundreds of meters per second to $<3 \text{ km s}^{-1}$, single-stage propellant (i.e., gunpowder) guns are usually the technology of choice for massive projectiles from a few to hundreds of grams total

weight. From about 2 to about 8 km s^{-1} , two-stage light gas guns are the most efficient means to launch massive projectiles. A few labs have explored three-stage guns to achieve higher velocities, up to $\sim 16 \text{ km s}^{-1}$. Electromagnetic rail guns have been applied in impact research mostly in the small particle range, due to the expense and difficulty of building and operating a rail gun for massive projectiles.

The two-stage light gas gun has been the critical technology enabling exploration of the pressure ranges relevant for terrestrial planet deep interiors (40–400 GPa); the design has evolved rather little since that described by Fowles et al. (1970). A schematic of a two-stage gun is shown in Figure 4. The first chamber or pump tube is prefilled with a few bars of hydrogen or helium gas. A calibrated rupture disk is placed in a central breech or accelerator reservoir between the pump tube and the second-stage barrel or launch tube. The second-stage projectile, generally a plastic sabot that tightly fits the inside of the barrel with a metal flier plate molded or pressed into the front, is placed downrange of the rupture disk. The launch tube, experiment tank, and catch tank are pumped to moderate vacuum ($\sim 0.1 \text{ torr}$). The detonation of a propellant charge drives a piston down the pump tube, compressing and storing potential energy in the hydrogen or helium. When the rupture disk breaks and the hydrogen or helium expands into the launch tube, it efficiently couples momentum to the second-stage projectile and achieves much higher velocity than is possible with direct propellant detonations. The velocity of the projectile may be measured before impact by a number of technologies, including double-flash x-rays, double-magnetic-induction velocity traps, breakwires, laser interrupts, and Doppler velocimetry (see PDV in the succeeding text).

In the most typical configuration, the front of a projectile consists of a flat, metal plate called a flier. This generates plane impact with a significant region of 1D strain. It also generates a supported or steady shock over the duration that it takes a backward propagating shock to reach the rear surface of the flier plate and then a forwards-propagating release wave to begin overtaking the shock front (see Figure 1). The ability of gun-driven plate impact experiments to achieve supported, flat-topped 1D shock events with durations up to a few

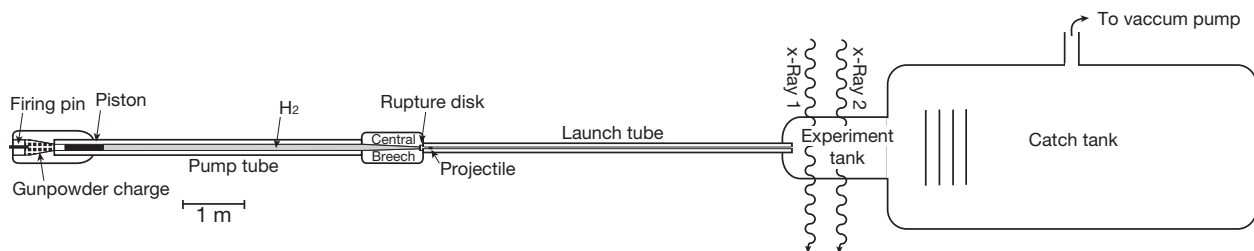


Figure 4 Schematic of a two-stage light gas gun (note 1 m scale bar), shown in a ready-to-shoot state. From left (uprange) to right (downrange), the parts are a remotely activated firing pin that is poised to ignite a primer and a main propellant charge of up to about 1 kg of gunpowder. This detonation will drive a plastic piston along the pump tube, which is prefilled with hydrogen (or helium) gas to a pressure of $\sim 1 \text{ MPa}$. As the light gas is compressed into the central breech (also called accelerator reservoir), it reaches a critical pressure ($\sim 300 \text{ MPa}$) at which the rupture disk bursts and allows the gas to expand into the smaller diameter launch tube (also called the barrel). A projectile, usually consisting of a plastic sabot backing a metal flier plate, weighing $\sim 20 \text{ g}$, has been tightly inserted into the barrel and is accelerated along the evacuated barrel and into the experiment tank. Here, its velocity is measured, for example, by a double-flash x-ray system, before it impacts a target and creates a shock wave event observed by various diagnostics. Finally, the projectile, target, hydrogen, and combustion gases all end up in the catch tank, which is large enough that the postshot condition is still below atmospheric pressure and can be safely pumped away.

microseconds is a key advantage, not presently available from other experimental configurations.

With certain modifications to experimental design, guns can also be used to study a range of alternative loading paths. For example, compound projectiles and layered targets can generate a multitude of multiple shock or shock-and-partial-release paths. A functionally graded impactor, with a nearly continuous gradient in density and shock impedance, can be used to generate a ramp wave for compression along the quasi-isentrope (Nguyen et al., 2006; Ray and Menon, 2009). Techniques are available to determine the velocity of release waves traveling into shocked material, in order to obtain sound speeds (Hixson et al., 1989; McQueen et al., 1982).

2.16.2.1.2 Explosives-in-contact

A classic method of generating strong shock waves is the detonation of high explosives in direct contact with the sample to be compressed. Shaped charges and controlled burn rates allow considerable control over the geometry, amplitude, and characteristics of the shock waves. These methods are reviewed in Ahrens (1987); they have been less important in geophysics research in the last few decades, but there remain applications (e.g., large-scale shock synthesis) for which explosive-in-contact is still the method of choice. The performance of typical explosives allows these methods to reach pressures up to tens of GPa. A special case, perhaps of historical interest only, is the achievement of TPa pressures through the use of underground nuclear tests to trigger subcritical detonation of fissile driver plates (Ragan et al., 1977).

2.16.2.1.3 Lasers

The most quickly growing area of shock compression science is the use of powerful lasers to drive shocks. The basic principle is the very rapid deposition of a large pulse of energy by an absorbing ablation surface, which is promptly transformed to a high-pressure plasma. This drives a shock forward into the sample as the plasma cloud expands backward into vacuum. Because the plasma absorbs the laser and because the plasma pressure drops as it expands, this technique naturally generates decaying shocks. The advantage of a decaying shock is that, as it propagates into a material and weakens, it probes in a single experiment a series of states along the Hugoniot rather than a single point. The disadvantage may be that it is less likely to achieve full equilibrium or phase transformation to a well-defined shock state. It is possible to generate a short supported shock event with a primary laser drive if the laser-driven shock causes a flier plate to detach from the rear of the initial target and fly across a gap to strike the final target (Swift et al., 2005); in fact, for launch velocities up to $\sim 5 \text{ km s}^{-1}$, this can be done with tabletop lasers rather than national-scale facilities (Brown et al., 2012). Furthermore, with tailoring of the shape of the laser pulse, lasers can also be used for quasi-isentropic compression experiments (Swift and Johnson, 2005).

A number of reviews have been written in recent years summarizing the state of the art in laser-driven shock compression (Paisley et al., 2008; Swift et al., 2004), but this is a rapidly evolving field. In the United States, facilities such as the OMEGA laser at the University of Rochester, the Jupiter/Janus laser at Lawrence Livermore National Laboratory (LLNL), and the National Ignition Facility at LLNL are making very high

energy densities and very strong shocks available to geoscience researchers. Studies on SiO_2 (Hicks et al., 2006) and MgO (McWilliams et al., 2012) have reached pressures of 1 and 1.4 TPa, respectively, and probed well beyond the melting range into dissociated and ionized liquid regions. Laser-driven shocks have also been combined with static precompression in diamond anvil cells and related devices in order to bring materials like H_2 , He, and H_2O to P - T states relevant to giant planet interiors (Loubeyre et al., 2004).

2.16.2.1.4 Magnetic drives

The discharge of a large capacitor bank through a closely positioned anode and cathode pair with currents flowing in opposite directions generates a powerful magnetic force that can be used to accelerate materials at high strain rates. These methods have been developed and applied to a number of materials at the Z-accelerator facility at Sandia National Laboratory in the United States. Directly driven compression from the magnetic force typically generates a ramp or quasi-isentropic compression (Caulle et al., 2002; Hall, 2000; Hall et al., 2001a; Reisman et al., 2001), though this can steepen into a shock after a short propagation distance. To date, this method has been most intensively applied to metals (Hayes et al., 2004; Jensen et al., 2006; Reisman et al., 2003; Rothman et al., 2005). Alternatively, the magnetic drive, like laser drives as discussed earlier, can be used to detach and accelerate a flier plate to generate a plane-wave impact and a supported shock (Chhabildas and Knudson, 2005; Hall et al., 2001b; Knudson et al., 2004; Lemke et al., 2005).

2.16.2.2 Diagnostics

Each of the technologies described earlier provides a means of generating shock or high-strain-rate compression of target materials. The next step in carrying out useful research with any of these facilities is diagnostics, that is, methods of characterizing the drive applied and the response of the target material during or after compression. Most of these methods involve the determination of velocity, either of the projectile, of shock or release waves in target materials, or of particle motion in target materials. Other methods mentioned here involve temperature determination, reflectivity at various wavelengths, and after-the-fact analysis of recovered specimens. There are a number of new diagnostic technologies under development that may become practical and routine in the near future, including transient x-ray diffraction of shocked samples (Suggit et al., 2010; Swift, 2008).

2.16.2.2.1 Pins

A simple and reliable technology for determining the time of an event at a known location is a pin or switch. Typically, a circuit that is open due to a small gap between conducting elements is held at some bias voltage, and a timing or recording device is set to detect the closure of the circuit. A single pin can be used as a trigger signal generator to enable other diagnostic or recording devices or experimental events whose timing depends on knowing the time and position of a projectile or shock wave. Multiple pins or switches can provide measurements of projectile or shock velocity if the initial separation in the projectile motion or shock propagation direction is

measured accurately. Tilt or bowing of projectiles or shock fronts can be diagnosed using multiple pins spaced perpendicular to the projectile motion or shock propagation direction. The timing resolution for all these approaches depends only on how precisely the pin closure event can be identified and recorded, the reproducibility of pin closure timing (involving issues such as repeatability of gap thicknesses from pin to pin), and the preexperiment metrology (determination of relative pin positions by precise measurement).

2.16.2.2.2 High-speed photography (flash, framing, and streak)

The relative timing of events, as well as their geometry and character, is often best determined using rapid image acquisition. Photography offers critical advantages over pins, gauges, and other signals that amount to isolated time series traces on oscilloscopes. Apart from the parallel, data-rich nature of image capture, it is often possible to diagnose experimental problems or identify patterns in image data that are not apparent in time series records. Photography is used in shock compression laboratories in several ways, often using repeat imaging or streaked imaging to identify and measure the velocity of moving objects or wave fronts.

Flash or double-flash photography enables precise determination of the state of an experimental system at a known moment in time, by combining a short pulse of x-rays or light with a continuously recording camera, film, or image plate. For example, in light gas gun labs, it is common practice to capture two x-ray images of the projectile in flight, at two known positions and times shortly before impact, in order to determine projectile velocity and simultaneously to characterize whether the projectile remains intact and to measure its tilt or other geometric characteristics. Velocity precision with baselines of tens of centimeters (known to the nearest micrometer) over times of tens of microseconds (known to the nearest few nanoseconds) can be of order 10^{-3} , or $\pm 1 \text{ m s}^{-1}$ for velocity of $\sim 1 \text{ km s}^{-1}$. Calibration of such a system depends on physical distance measurement, parallax and magnification corrections in some cases, and an accurate time-base for recording the time between flash discharges.

Framing cameras repeatedly and rapidly acquire images of a scene and can be used to visualize or animate dynamic processes and to measure velocities of projectile motion or shock propagation by comparison of successive images. Cameras with a range of spatial and spectral resolutions, framing rates, and number of frames in a sequence are available, extending in some cases to 1 billion frames per second (i.e., spatial resolution of nanoseconds). Framing cameras are standard tools in studies of impact and cratering processes. Calibration of framing cameras can be achieved in a number of ways, including interference imaging of a known frequency signal.

Streak cameras typically capture a single image in a time-transgressive fashion, representing changes over time in light intensity along a slit or line perpendicular to the streak direction. Spatial resolution along the slit is determined by pixel density and quality of focus in one axis, whereas temporal resolution is determined by slit width, pixel density, and quality of focus along the perpendicular axis as well as streak rate. Classical streak camera designs using rapidly rotating mirrors or prisms have given way in recent decades to electronic streak

cameras in which incoming light is converted to an electron beam, steered by the application of electric fields, and converted (e.g., by phosphor screen) back into light or another signal to which the film or imaging chip is sensitive. Streak camera records are often calibrated against time using radio-frequency standards (Figure 5(a)).

In all these instances of the use of photography, recent decades have seen the replacement of film-based image capture with digital technologies. Fast, sensitive, high-resolution, and large-area imaging chips including charge-coupled devices (CCDs) and complementary metal-oxide-semiconductor offer in many cases clear advantages over film. These include the possibility of rapid repeat imaging; instant readout; digital image processing; and ease of data transfer, storage, and archiving. Furthermore, many specialty films previously used in shock wave labs are no longer available from the manufacturers as film use and production have declined worldwide in favor of digital photography. In some applications, the optimal solution involves an intermediate stage whereby a photosensitive image plate may store an image for later digital acquisition by a dedicated scanner.

2.16.2.2.3 Velocity gauges

Photographic methods are usually best for determining projectile velocities and shock arrival times at visible surfaces. For the direct determination of shock transit times inside a target material, for the measurement of particle velocity within a target, and for wave velocity profiles extending in time beyond the first arrival of a shock wave, other technologies are available that do not depend on visual line of sight to the point of measurement. Velocity gauges are sensors that can be embedded within a material or between slabs of target material for *in situ* determinations of stress or velocity.

A particularly simple and effective application of *in situ* gauges in shock and dynamic compression research is based on embedded wire loops in a nonconducting sample, placed inside Helmholtz coils or other means of generating a magnetic field with field lines threading the embedded loops. In this geometry, the motion of a wire loop along the magnetic field lines generates a displacement current in the loop that can be readily measured as a function of time. The arrival time of the onset of motion at successive loops with known initial position provides a shock or Lagrangian wave velocity, whereas the amplitude of loop velocity is a direct measurement of particle velocity. Detailed profiles of particle velocity as a function of time can record multiple-wave structures due to elastic/plastic effects and phase transitions or characterize multiple shock or shock-and-partial-release paths (Figure 5(b)). It should be emphasized that the amplitude of the loop current is a direct measurement of velocity, as opposed to methods discussed in the preceding text that estimate velocity by finite difference of multiple determinations of position across time. This method has been used in materials including water ice (Stewart and Ahrens, 2005).

2.16.2.2.4 Interferometry (velocity interferometry system for any reflector/photonic Doppler velocimetry)

Interferometry refers to any method that depends on the superposition of waves to determine distances or velocities on the scale of the wavelength of a probe signal. Classical Michelson

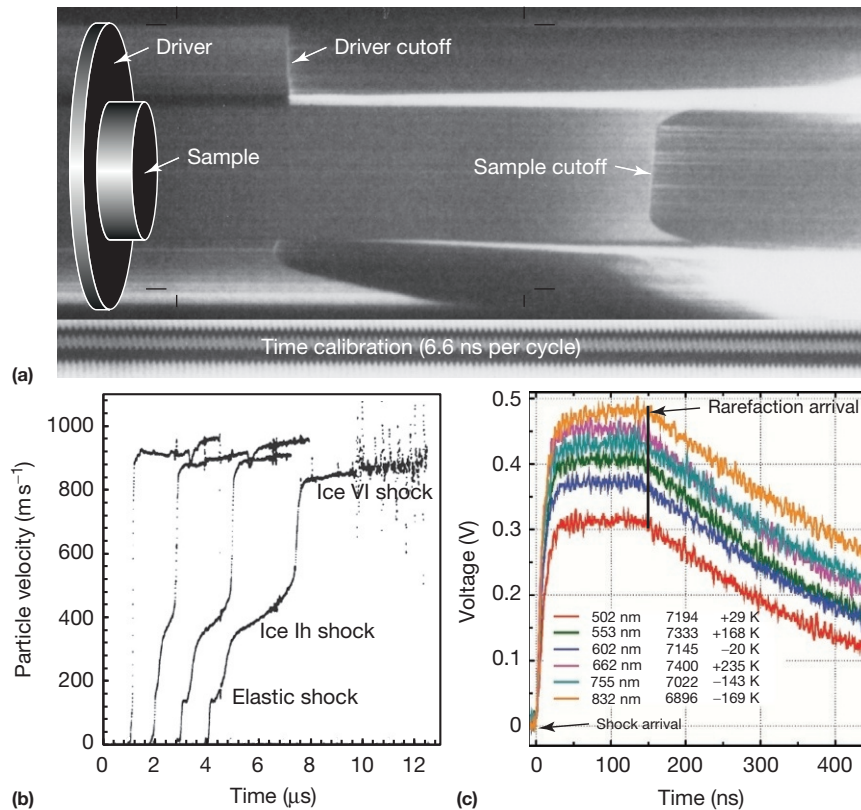


Figure 5 Examples of raw data from several shock diagnostics. (a) A streak camera image for measurement of shock velocity (reproduced from Asimow PD, Sun DY, and Ahrens TJ (2009) Shock compression of preheated molybdenum to 300 GPa. *Physics of the Earth and Planetary Interiors* 174: 302–308). The target geometry is shown at left; it consists of a driver plate with a cylindrical sample mounted on the downrange side. After impact, a shock wave propagates through driver and then through sample. Light is reflected off the back of the target, through a narrow slit, forming a line on the film or CCD; this line is swept quickly across the image plane, creating a time axis (time increases to the right). Streak rate is calibrated using the radiofrequency oscillator shown at the bottom of the image. The primary measurement is the time elapsed between the shock exiting the driver and, somewhat later, exiting the sample. With sample thickness, this yields shock velocity. (b) The use of four embedded wire-loop velocity gauges to observe multiple-wave structure, particle velocity, shock velocity, and material strength in 100 K water ice (reproduced from Stewart ST and Ahrens TJ (2005) Shock properties of H₂O ice. *Journal of Geophysical Research-Planets* 110: 03005). The four traces show particle velocity at original positions 0, 3.3, 7.5, and 11.8 mm downrange from the impact face. The first gauge shows a simple shock. With increasing distance, three waves are seen to disperse. The first and fastest is an elastic wave with stresses equal to the Hugoniot elastic limit (related to yield strength); the second is a plastic shock traveling in the normal ice crystal structure ice Ih; the third and slowest wave accomplishes a phase transition to the dense ice VI structure. Time between wave arrivals at subsequent gauges yields Lagrangian wave speed. (c) Intensity traces from a six-channel optical pyrometer for measurement of shock temperature and sound speed in MgO (reproduced from Fat'yanov O, Asimow P, and Ahrens T (2011) Thermodynamics of MgO shocked to 250 GPa and 9000 K. *Bulletin of the American Physical Society* 56). At time 0, the shock passes from the opaque driver into the transparent sample and light emission rapidly rises to a plateau, which is maintained until (at ~150 ns) a rarefaction wave overtakes the shock and begins to attenuate the shock pressure and temperature. Previous observation of a calibrated standard lamp with the same instrument in the same geometry allows each trace to be converted to an absolute intensity and hence a temperature; uncertainty resulting from dispersion among the channels is shown in the figure.

interferometers combine a direct and a counter-propagating reflected signal in order to form a standing wave, which changes from destructive to constructive interference and hence from amplitude minima to maxima over one-half wavelength. Applications in dynamic compression research typically involve technologies to precisely and quickly measure velocities rather than positions, and this is achieved in two ways: velocity interferometry system for any reflector (VISAR) and photonic Doppler velocimetry (PDV, also called heterodyne velocimetry or DISAR).

VISAR is an older and more established technology, primarily because it requires much lower data sampling rates. A VISAR differs from a conventional displacement interferometer due to

the placement of a delay element in one leg of the optical path. When a prompt reflection is interfered with a delayed reflection from the same surface, fringes arise due to the motion of the reflector over time. Hence, the number of fringes detected counts changes in the velocity of the reflector rather than its position. This technique was made practical for many applications in dynamic compression when Barker and Hollenbach (1972) discovered that diffuse rather than specular reflections could be used if the two legs of the interferometer have the same physical path length, differing only in optical path length through the use of an etalon (a material with index of refraction, hence speed of light, different from air) to achieve the delay. In typical applications, VISAR is carried out with visible

wavelength lasers such as the Ar-ion laser at 512 nm. VISAR signals can be recorded from a single reflecting point or a series of points using one or more focused laser spots. Velocity along a reflecting line can also be imaged using a streak camera to capture fringe position versus time; such a configuration is also called an optically recording VISAR (ORVIS). One disadvantage of the VISAR is that the 2π periodicity of signal phase can translate into more than one velocity corresponding to a given fringe position, in cases where the rapid acceleration at the arrival of a shock front makes it impossible to continuously trace recorded fringes. This can be overcome using more rapid recording or by combining two VISARs with different fringe constants. VISAR reflections are frequently measured from an interface between an opaque sample and a transparent window, rather than from a free surface against vacuum. In this case, there is a correction for the index of refraction of the window material, which has been calibrated for several common windows, for example, LiF (LaLone et al., 2008).

An useful additional measurement that results especially from ORVIS data is the amplitude (as opposed to the phase) of the reflected signals, which gives information on the optical reflectivity of the shocked material and hence on its electrical conductivity or degree of ionization. Such data collected from strong laser-driven shocks have been used to infer metallization or ionization of liquid H_2 (Loubeyre et al., 2004), H_2O (Celliers et al., 2004), SiO_2 (Hicks et al., 2006), and MgO (McWilliams et al., 2012), among other materials.

A rather new development in velocity measurement in dynamic compression experiments is PDV. This is an application of direct Michelson interferometry combined with data recording sufficiently rapid as to capture the passage of interference fringes due to changes in reflector position at velocities of kilometers per second. Using an infrared laser with wavelength near $1.5\ \mu m$, capturing velocities up to $10\ km\ s^{-1}$ requires data sampling rates of 20 GHz. Standard PDV systems can be difficult to set up and align since a stationary reflecting surface generates no signal; improved systems are available that detune one of the interfering signals slightly to achieve a finite beat frequency for stationary reflectors. PDV does not suffer from the cyclic ambiguity in velocity that affects VISAR systems. The accuracy and precision of PDV and the corrections for observation of a reflecting interface through a transparent window are discussed by Jensen et al. (2007).

2.16.2.2.5 Pyrometry

The diagnostic techniques so far discussed are all aimed at the determination of wave arrival times and velocity measurements. Another major area of diagnostic technology applies to the measurement of temperature during dynamic compression experiments. This includes both shock temperature (at a point on the Hugoniot or continuously along the Hugoniot) and postshock temperature (after quasi-isentropic release to low or ambient pressure). The simultaneous measurement of shock velocity, particle velocity – and hence internal energy from the third Rankine–Hugoniot equation – and temperature yields a determination of the isochoric heat capacity of the shock-compressed material, which often differs substantially from the classical high-temperature Dulong–Petit limit. Phase transitions along the Hugoniot may be revealed by latent heat

anomalies, both in comparison of discrete Hugoniot points (Lyzena et al., 1983) and along decaying shock paths (Hicks et al., 2006; McWilliams et al., 2012). Postshock temperature reveals the entropy increase due to irreversible work and may also demonstrate phase transitions in the shock or recovered state (Boslough, 1988; Stewart et al., 2008).

Temperature of dynamically compressed materials is most often measured with pyrometry, that is, the analysis of the brightness and/or spectral shape of thermally emitted radiation (McQueen and Fritz, 1982). This is simplest in the case of transparent materials, where as a shock propagates through the sample, radiation from the shocked region can be observed through the remaining unshocked sample. In this case, the time-resolved measurement of radiation intensity at a particular wavelength channel can be fitted to determine the linear absorption coefficient (and hence, by Kirchhoff's law, emissivity) of the shocked material, the linear absorption coefficient of the unshocked material, and the blackbody temperature (Luo et al., 2004). Shock temperatures can also be studied in opaque materials using a transparent window such as LiF or Al_2O_3 (Holland and Ahrens, 1998; McQueen and Isaak, 1990) and observation of the radiation from the sample–window interface. In this case, the time-resolved measurement of radiation intensity is a complex function of the shock temperature in the opaque material, the shock temperature in the window, the reshock or partial release temperature in the opaque material, and the relative thermal diffusivities of the two materials (Grover and Urtiew, 1974; Nellis and Yoo, 1990; Tan and Dai, 2001). When the sample–window impedance match state keeps the sample in a partially molten condition, the interface temperature may be buffered to a point on the melting curve (Tan et al., 2005). Despite these complexities, many influential results on, for example, shock and melting temperatures in iron, its alloys, and other metals have been determined by interface temperature measurement (Anderson and Ahrens, 1996; Dai et al., 2009; Williams et al., 1991). See in the following text under Phase Transitions and Metals (Section 2.16.3.2.2) for a discussion of controversies that have surrounded results of this type of measurement.

A number of pyrometer designs have been used in shock, postshock, and interface temperature measurements. Most results until recently used multichannel optical to near-infrared pyrometry with a few (4–6) narrow band-pass filter channels (Boslough and Ahrens, 1989; Lyzena and Ahrens, 1979) measured by photomultiplier tubes or photodiodes and recorded on digital sampling oscilloscopes (Figure 5(c)). There are a number of choices as to how to analyze such data to extract temperature. If an absolute brightness calibration is available, from a standard lamp or a shock temperature on an accepted reference material, then each channel may independently yield a temperature based on its brightness relative to the standard. Alternatively, depending on spectral coverage, multichannel data can be fitted to a gray body model and temperature extracted from the spectral shape. More recently, especially in laser-driven shock experiments that reach very high temperatures and require very high time-resolution, single-channel streaked optical pyrometry – that is, unfiltered total brightness recorded as light intensity on a streak camera record – has become practical due to high bit-depth digital streak camera recording (Miller et al., 2007; Morita et al., 2011).

2.16.2.2.6 Postmortem analysis

Although it is not the primary focus of this chapter, it bears mentioning that some dynamic compression experiments are designed so that the sample can be recovered and analyzed after the experiment. With the leisure of sample preparation and unlimited measurement time, methods including optical microscopy, scanning and transmission electron microscopy, x-ray diffraction, infrared and Raman spectroscopy, and many others can be applied to characterizing the phase assemblage and physical–chemical properties of recovered materials. The field of shock recovery is reviewed in Davison et al. (2003). Techniques for sample recovery range from embedding the sample within a chamber sufficiently massive to survive the impact intact (Sekine, 1997; Sekine et al., 1987) to conducting the impact within a cavity lined with foam, gel, or other materials intended to gently stop and retain ejecta fragments. Shock recovery experiments form an important complement to observations of naturally shocked impact craters and meteorites in the study of high-pressure shock metamorphism and melting (Stoffler and Langenhorst, 1994). However, critical aspects of natural shock metamorphism are extremely difficult to reproduce in the laboratory, especially the long durations of shock events driven by collisions of large objects (e.g., Xie et al., 2001). Samples embedded in high-impedance chambers also typically experience shock reverberation rather than a single-shock event, and recovery of high-pressure phases and melt structures is impeded by the high postshock temperatures (and hence, extensive low-pressure annealing) to which these materials recover upon release (e.g., Shimoda et al., 2004).

2.16.2.3 Interpretation, Modeling, and Postprocessing

In some cases, the raw data records collected during dynamic compression experiments do not directly or immediately provide the material properties that one desires to measure. Instead, the raw data may need to be processed or used as constraints on a modeling exercise in order to reach a final answer. Hence, under experimental techniques, it is appropriate to discuss some of the strategies that have been adopted to convert dynamic measurements into desired quantities. A good example is experiments that measure free-surface velocities, for example, by VISAR or PDV, with intent to constrain shock states within the volume of an opaque material under shock loading and release. Only the free surface (or, in some cases, a reflecting surface between the material of interest and a buffer or window) can be observed, but as the waves reach the free surface, the particle velocity changes and so free-surface velocity is not a direct measure of the shock state away from the surface. In the simplest cases, the so-called free-surface approximation presumes that the release path follows the Hugoniot, in which case the free-surface velocity is just twice the particle velocity in the interior of the shocked material. However, the free-surface approximation fails in a number of cases, when irreversible processes such as porosity collapse, phase transitions, and elastic/plastic effects occur on shock or on release (e.g., Barker and Hollenba, 1974). In such cases, the method of characteristics is available to integrate the equations of motion backward in time and space to constrain the particle motion inside the sample (Hayes, 2001; Maw, 2004).

2.16.3 Geophysical Applications

2.16.3.1 Equations of State and Phase Transitions

Much of high-pressure mineral physics is dedicated to determining the EOS – the functional relationship between density (or volume), pressure, and temperature (or energy or entropy) of naturally occurring materials—rocks, minerals, and fluids – in order to support geophysical inferences about the composition, thermal state, mineralogy, and dynamics of planetary interiors. Dynamic compression methods have played an essential part in such EOS determinations, because they reach the full range of pressure conditions relevant for terrestrial planets and because pressure and density are naturally and accurately determined by these methods. There are, however, some limits to what can be done with dynamic methods alone and hence also a need for integration with complementary techniques. At low pressures, below and somewhat beyond the Hugoniot elastic limit, strength effects prevent shock experiments from measuring the hydrostatic EOS (Asay and Lipkin, 1978). In materials that undergo phase transitions, it may not be possible to obtain shock data on the equilibrium phase of interest at particular conditions and it may be uncertain in some cases what phase is being observed experimentally. At higher pressures, the large temperature increase along the Hugoniot may take shock compression conditions far above the temperatures of direct relevance to planetary interiors, requiring often model-dependent thermal pressure corrections. However, ways of obtaining data off the principal Hugoniot are described earlier and their applications to geophysics cited later.

Equations of state apply to particular phases as well as compositions. In order to predict the geophysical behavior of some composition, it is necessary to know what phase or mixture of phases are present, as well as the EOS, elasticity, and other physical properties of those phases. Hence, it is difficult to fully separate the discussion of EOS from the subject of phase transitions. A convenient way to summarize behavior of a composition or a family of compositions over some range of conditions is a *phase diagram*, a map of the thermodynamically stable phases or phase assemblages as functions of, for example, pressure and temperature (for instance, Figure 6(a)). The boundaries on phase diagrams are phase transitions. A number of phase transitions are of first-order importance in geophysics, including both melting and formation of high-pressure polymorphs (Chapter 2.03). With increasing pressure, for example, pyroxenes transform to high-pressure pyroxene-like structures and then in sequence to akimotoite, majorite, perovskite, and postperovskite structures. Olivine transforms to wadsleyite, then to ringwoodite, and finally decomposes to perovskite and oxide. Iron transforms to denser forms, probably ϵ -Fe (hcp structure) in the inner core.

Dynamic compression methods are not ideal for locating subsolidus equilibrium phase transitions; transitions occur too far from equilibrium in these experiments. They can indicate the presence of phase transitions or decompositions and constrain the EOS of high-pressure phases, but further work with other methods is then required to identify the new phases and define the equilibrium relations. However, melting is a special case. It may be useful to locate melting curves even approximately when

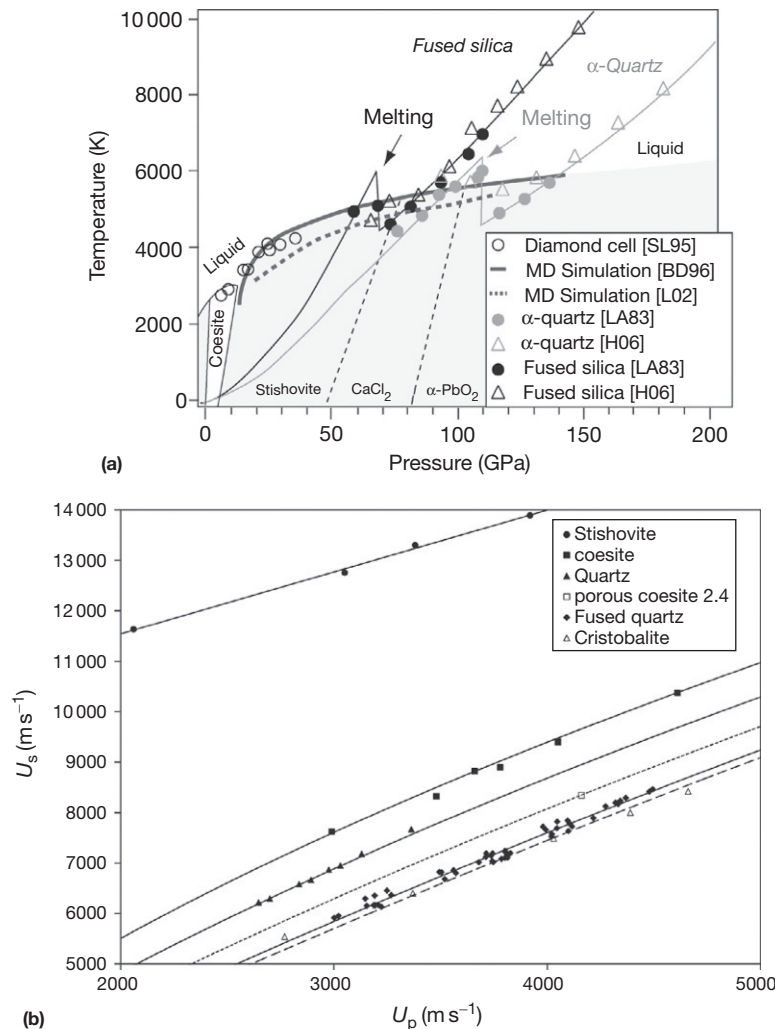


Figure 6 (a) Pressure–temperature phase diagram of SiO₂ system in the terrestrial mantle pressure range, constrained by shock experiments and other results. References abbreviated in legend are LA83 (Lyzena et al., 1983), SL95 (Shen and Lazor, 1995), BD96 (Belonoshko and Dubrovinsky, 1996), L02 (Luo et al., 2002a), and H06 (Hicks et al., 2006). The drops in temperature along the Hugoniot of alpha-quartz and fused silica indicate crossing from the superheated solid regime into the liquid regime and therefore approximate the melting curve; melting temperatures inferred by this method show reasonable agreement with molecular dynamics simulation results and extrapolation of direct melting determinations in the laser-heated diamond anvil cell. (b) Shock equation of state measurements in the shock velocity–particle velocity plane for various initial phases and porosities of SiO₂, all considered to be shocked into the stability regime of stishovite. The line through the initially stishovite data is a simple linear regression, since no phase transition has occurred for these data. All the other lines are model calculations based on the transition energy between the starting phases and stishovite as well as a Mie–Grüneisen thermal pressure correction using the volume dependence of the Grüneisen parameter of stishovite. Data from Luo et al. (2002b), Lyzena et al. (1983), Marsh (1980), McQueen et al. (1963), Podurets et al. (1981) and Trunin et al. (2001).

there are no other constraints. There are limits to the extent to which melting transitions can be overdriven before homogeneous nucleation causes melting even on a shock timescale (Luo and Ahrens, 2003, 2004; Luo et al., 2003). Some materials appear to follow a family of Hugoniot states that map out equilibrium melting behavior: with increasing pressure, a subsolidus region, a partially molten set of points restricted to the melting curve, and a superliquidus region. Other materials display clear superheating: with increasing pressure, a subsolidus region, a metastable solid region, and then a more or less sudden drop in shock temperature and sound speed to a fully molten region. The location of complete melting can be inferred by interpolation

between the highest-pressure superheated solid state and the lowest-pressure liquid Hugoniot point. In a decaying shock experiment, continuous sampling of this interval may display a well-defined minimum in temperature. Hence, even in the presence of nonequilibrium melting behavior (i.e., superheating), the location of the melting curve can be defined or at least constrained using dynamic compression methods (Chapter 2.22).

2.16.3.2 Minerals

The Hugoniot of a number of mantle phases have been studied and phase transitions observed. Although, as discussed

earlier, it is challenging to define equilibrium phase relations among solid phases by this method, the data can be shown to be consistent with known phase diagrams and then to provide additional constraints on the properties of high-pressure phase assemblages.

The melting curves of a number of minerals have been defined or at least constrained using dynamic compression methods. This includes the key end-members silica, forsterite and enstatite (MgSiO_3), and mantle composition (Fo_{90}) olivine.

2.16.3.2.1 SiO_2

A number of authors have reported Hugoniot and shock temperature data for various starting materials in the SiO_2 system, across a wide pressure range extending up to 1.4 TPa. Akins and Ahrens (2002) assigned the data available at that time to phase regimes and found that the principal Hugoniot of α -quartz passed through elastic (to 5–15 GPa, depending on orientation), deformational quartz (to 23 GPa), mixed-phase (to 43 GPa), stishovite (to 70 GPa), CaCl_2 structure (to 115 GPa), and melt regimes. Melting at 115 GPa and 4900 K is confirmed by the shock temperature data of Lyzenga and Ahrens (Lyzenga et al., 1983), which also show that the Hugoniot of fused quartz ($\rho_o = 2204 \text{ kg m}^{-3}$) crosses into complete melting at 75 GPa and 4600 K. These melting temperatures were confirmed by the decaying shock temperature data of Hicks et al. (2006); see Figure 6(a). The very high-pressure behavior of silica liquid was most recently studied both using Z-accelerator plate impact experiments and quantum molecular dynamics calculations by Knudson and Desjarlais (2009), who propose a significant revision to the Hugoniot of Hicks et al. The subsolidus phase diagram, melting curve, and progressive behavior of liquid into the warm, dense matter regime are all therefore well constrained for SiO_2 .

The high-pressure phase stishovite, or rutile-structured SiO_2 , is found in impact craters into quartz-bearing rocks (Chao et al., 1962) and in shocked meteorites (El Goresy et al., 2004). Although it has proven difficult to recover stishovite from laboratory-scale impact recovery experiments (but Tschauner et al. (2006) suggest the amorphous material often found in such experiments is decompressed from stishovite), stishovite does seem to occur over a significant pressure range on the Hugoniots of many starting phases and densities of silica, ranging from stishovite itself ($\rho_o = 4.29$, synthesized and shocked by Luo et al. (2002b)) to coesite ($\rho_o = 2.92$, (Luo et al., 2002b; Podurets et al., 1981)), α -quartz ($\rho_o = 2.65$, (Marsh, 1980; Trunin et al., 2001)), porous coesite ($\rho_o = 2.40$ (Podurets et al., 1981)), fused quartz ($\rho_o = 2.204$, (Lyzenga et al., 1983; Marsh, 1980; McQueen et al., 1963; Trunin et al., 2001)), and cristobalite ($\rho_o = 2.13$, (Podurets et al., 1981)). Luo et al. (2002b) showed that the data on stishovite, coesite, and quartz each shocked into the stishovite regime constrained the volume dependence of the Grüneisen parameter of stishovite to $\gamma_o = 1.35$ and $q = 2.6 \pm 0.2$ (see eqn [9]). Figure 6(b) shows an expanded evaluation of this model, where a straight-line fit to the principal Hugoniot of stishovite ($C_o = 9080 \text{ km s}^{-1}$, $s = 1.227$), and Mie-Grüneisen thermal pressure correction with the Grüneisen parameter fit of Luo et al. (2002b) is used to compute the stishovite regime segments of the Hugoniots of all the lower-density starting

materials with remarkable agreement. This result can be taken as confirmation that the functional form selected for the volume dependence of γ works well for stishovite between densities of 4000 and 6000 kg m^{-3} and also as confirmation of the assignment of the selected data to the stishovite regime.

2.16.3.2.2 MgSiO_3

The magnesium metasilicate composition is a reasonable approximation of the bulk composition of the Earth's mantle and contains the most abundant stoichiometric phase of the lower mantle, MgSiO_3 perovskite. Hence, it is an essential simplified model system for mineral physics studies addressing the Earth's mantle and those of other terrestrial planets as well. Several studies agree that enstatite, whether pure MgSiO_3 or containing 10–15 mol% FeSiO_3 and perhaps minor Al_2O_3 components, transforms to perovskite structure along the Hugoniot (Ahrens and Gaffney, 1971; Jeanloz and Ahrens, 1977; Watt and Ahrens, 1986), and hence, shock wave data have been fit to obtain the EOS of MgSiO_3 perovskite (e.g., Gong et al., 2004). There is also an abundance of static compression data on the various phases of MgSiO_3 , which however leave certain ambiguities due to disagreement among studies and lack of constraint on the internal energy in such experiments. The work of Mosenfelder et al. (2009) included new Hugoniot data on presynthesized MgSiO_3 targets containing mostly perovskite structure with minor majorite (garnet) structure, as well as an attempt at synthesis of all existing shock and static data on the equations of state of MgSiO_3 perovskite, postperovskite (CaIrO_3 structure), and melt. The pressure of melting along the Hugoniots of enstatite glass (Akins et al., 2004; Luo et al., 2004; Mosenfelder et al., 2009), single-crystal enstatite (Akins et al., 2004), porous enstatite (Simakov and Trunin, 1973), and ultraporous oxide mix (Marsh, 1980) is well established in each case, but the temperatures at these melting points remain uncertain – either they were not measured (and estimated shock temperatures depend on model parameters) or there are uncertainties of several hundred Kelvin on the data (Akins et al., 2004; Luo et al., 2004). Nevertheless, the melting temperature along the principal Hugoniot of single-crystal enstatite inferred from shock temperature experiments – 5300 K at the Earth's core–mantle boundary pressure of 135 GPa – agrees well with estimates from ab initio molecular dynamics (Stixrude and Karki, 2005). Recent laser-driven shock results on both MgSiO_3 glass and enstatite crystal starting materials (Spaulding et al., 2012) are consistent with the previous gas gun temperature results, extend the temperature data to 450 GPa, and reveal an apparent liquid–liquid phase transition at very high pressure, but do not substantially improve the constraints on the melting curve itself. The most complete synthesis currently available of the MgSiO_3 melting relations at terrestrial mantle pressures, from ab initio simulation results and constraints from dynamic and static compression experiments, is given by de Koker and Stixrude (2009).

2.16.3.2.3 Mg_2SiO_4

Since olivine is the dominant mineral phase of the Earth's upper mantle, with important phase transitions defining the 410 and 660 km seismic discontinuities, it has also been a major target of shock wave study, with substantial datasets on

EOS both of natural compositions and synthetic forsterite (Brown et al., 1987; Jackson and Ahrens, 1979; McQueen, 1968; Mosenfelder et al., 2007; Syono et al., 1981a,b; Watt and Ahrens, 1983); sound speed bracketing the melting transition (Brown et al., 1987); and selected shock temperature results, again on both natural (Holland and Ahrens, 1997) and synthetic (Lyzenga and Ahrens, 1980) compositions. The melting point inferred – about 4000 K at 135 GPa (Luo et al., 2004) – is interpreted as a eutectic between perovskite and periclase and therefore a reasonable approximation to the solidus of most plausible lower mantle compositions. It is therefore lower than the melting point of perovskite inferred from shock temperature or ab initio calculations but is in good agreement with the solidus of either peridotite (4180 K, Fiquet et al., 2010) or chondrite (4150 K, Andraut et al., 2011) compositions observed by *in situ* laser-heated diamond anvil cell methods and with the calculation of the binary MgO–MgSiO₃ phase diagram given by de Koker et al. (2013).

2.16.3.2.4 MgO

A final major component of terrestrial mantles are nonsilicate oxides, which are minor components in crustal rocks but become significant beyond the stability limits of orthosilicate phases (660 km, on Earth). The most widely studied and abundant is MgO, representative of one end-member of the MgO–FeO (periclase–ferropericlase–magnesiowüstite–wüstite) solid solution series. Its Hugoniot has been reported (Ahrens, 1966; Duffy and Ahrens, 1995; Marsh, 1980; Vassiliou and Ahrens, 1981) and compares well with static EOS data (Dewaele et al., 2000; Fiquet et al., 1999; Speziale et al., 2001) and simulations (Karki et al., 1997). A coherent *P*–*V*–*T* EOS for the B1 phase of MgO can be put together from shock and static data and used as a pressure standard in static experiments (Jin et al., 2010). There is, however, some uncertainty surrounding the subsolidus phase diagram (Aguado and Madden, 2005; Zhang et al., 2008) and extreme disagreement concerning the melting curve. Static determination of the melting curve in the laser-heated diamond anvil cell yields a very flat melting curve, extrapolating to ~5000 K at the core–mantle boundary (Zerr and Boehler, 1994), whereas analysis of the FeO–MgO binary melting loop at pressures up to a few GPa suggests an extremely steep melting curve for MgO, exceeding 5000 K already at 10 GPa (Zhang and Fei, 2008). Numerous ab initio and empirical molecular dynamics theoretical studies have reported estimates of the melting curve of MgO at high pressure and they occupy much of the range between these two experimental determinations (Alfe, 2005; Belonoshko and Dubrovinsky, 1996; Belonoshko et al., 2010; Cohen and Gong, 1994; Cohen and Weitz, 1998; de Koker and Stixrude, 2009; Liu et al., 2006; Ohtani, 1983; Strachan et al., 1999; Voadlo and Price, 1996). Shock studies did not contribute until recently to the debate on the melting curve of MgO because it occurs at such high temperature that light gas gun experiments on single-crystal MgO do not reach the melting curve (e.g., Svendsen and Ahrens, 1987). However, recent shock temperature studies using both strongly preheated targets in light gas gun experiments (Fat'yanov et al., 2009, 2011) and extremely high-pressure decaying laser-shock experiments (McWilliams et al., 2012) support a melting curve passing through about 8000 K at the Earth's core–mantle boundary,

similar to the results of the most recent ab initio molecular dynamics studies (Belonoshko et al., 2010; de Koker and Stixrude, 2009). The situation is summarized in Figure 7, which shows that the shock wave data at this time provide only a strong lower bound on the melting curve, excluding the extrapolations of the Zerr and Boehler (1994) data and the models of Strachan et al. (1999) and Belonoshko and Dubrovinsky (1996) but probably allowing all the other models.

2.16.3.3 Rocks

Shock compression of whole rocks, that is, aggregates of one or more minerals with or without some porosity, is of direct importance for cratering studies and for understanding the effects of conventional and nuclear explosions. Such studies also constrain the EOS and elastic properties of the crust and mantle. Much early work in both the United States and Russia focused on Hugoniot studies of rocks (Ahrens and Gregson, 1964; Ahrens and O'Keefe, 1972; Anderson and Kanamori, 1968; Lombard, 1961; Marsh, 1980; McQueen et al., 1967; Nakazawa et al., 1997; Trunin et al., 2001). More recently, it has become more common to focus experimental studies on single minerals and to rely on mixing models to estimate aggregate rock properties from mineral data (Gavrilyuk and Saurel, 2007; Krueger and Vreeland, 1991; Petel and Jette, 2010). Some properties beyond the Hugoniot and EOS, such as fracture formation and damage, are hard to estimate from mixing relations and still rely on experiments on natural rocks and composites (Ai and Ahrens, 2004, 2007).

2.16.3.4 Metals: Iron and Terrestrial Planet Cores

Many studies have characterized the shock compression behavior of metals, and this has been essential to their use as flier plates and hence impedance standards for compression of other materials of geophysical interest (McQueen and Marsh, 1960, 1966; Mitchell and Nellis, 1981; Molodets, 2005; Nellis et al., 2003; Ragan et al., 1977; Walsh et al., 1957). Of course, Fe is of distinct and unique importance because it dominates the Earth's core (Chapter 2.06).

Perhaps the most critical contribution that dynamic compression has made to Earth science is the confident and accurate determination of the density of Fe liquid and solid phases at core pressures and temperatures, and hence – by comparison with the geophysically determined density of the Earth's core – the discovery and quantification of the core density deficit and the need for light elements in the core. Birch (1952), armed only with preliminary density models for the core and static compression data, only suspected that the outer core is less dense than Fe or Fe–Ni liquid. On the other hand, Birch (1964), having both refined seismic density models and access to the Hugoniot data of McQueen and Marsh (1960) and Al'tshuler et al. (1960), confidently assigned a difference of 10% and was able to then begin speculating on the identity of light alloying elements such as silicon, oxygen, or sulfur (see, e.g., Poirier, 1994). Continuing refinements of both static (Antonangeli et al., 2010; Hirao et al., 2004; Ma et al., 2004; Murphy et al., 2011; Nishida et al., 2008; Sanloup et al., 2004) and dynamic experimental compression methods (Ahrens,

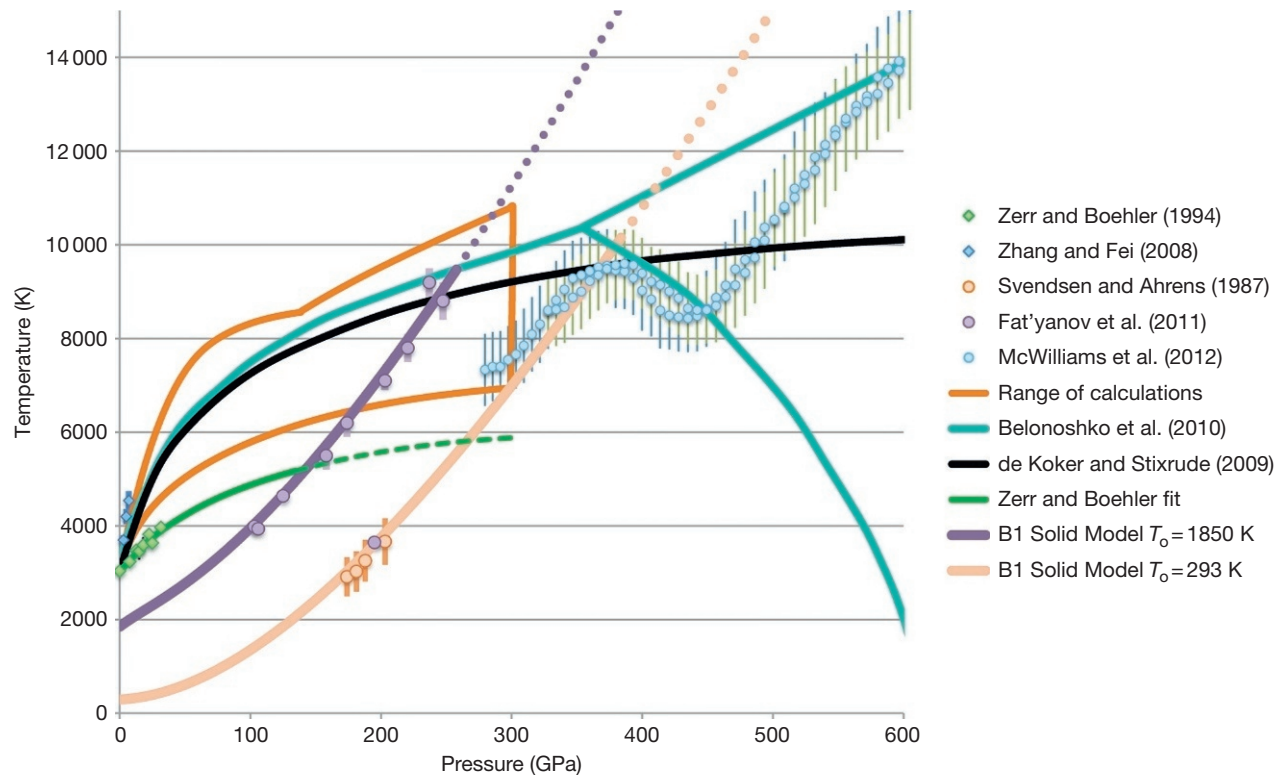


Figure 7 Phase diagram of MgO with various experimental and computational estimates of the melting curve. Experimental data include determinations of the melting curve (diamonds) and shock temperature measurements (circles; two different experiments by McWilliams et al. (2012) are shown); the Zerr and Boehler (1994) measurements are extrapolated using a Lindemann law. Calculated melting curves are shown from nine different studies using various levels of ab initio and empirical molecular dynamics (the orange envelope shows upper and lower bounds that encompass all studies not explicitly plotted (Alfè, 2005; Belonoshko and Dubrovinsky, 1996; Cohen and Gong, 1994; Cohen and Weitz, 1998; Liu et al., 2006; Ohtani, 1983; Strachan et al., 1999)). The B1–B2 solid phase transition boundary estimated by Belonoshko et al. (2010) is shown, as this transition appears to have a major effect on the decaying shock temperatures observed by McWilliams et al. (2012). Calculated shock temperatures are shown along the principal Hugoniot ($T_0 = 293$ K) and the preheated Hugoniot ($T_0 = 1850$ K) of B1 solid MgO, using parameters calibrated to the offset between cold and hot shock velocities by Fat'yanov et al. (2009); the metastable superheated segments of these Hugoniots are shown dotted. Where the shock temperature data agree with these model curves, it is argued that the phase present in the shock state is in fact solid B1 MgO; hence, the Fat'yanov et al. (2011) data are all consistent with solid and provide only a lower bound on the melting curve. There is an anomaly in apparent heat capacity in the McWilliams et al. (2012) data at 600 GPa (not readily visible in T – P space), consistent with the Belonoshko et al. (2010) melting curve of B2 phase.

1982; Ahrens et al., 2002; Anderson and Ahrens, 1994; Chen and Ahrens, 1995; Huang et al., 2011; King and Ahrens, 1973) and of quantum computational methods (Alfè et al., 2002; Steinle-Neumann et al., 1999; Stixrude et al., 1997; Vocadlo, 2007) have refined both the density and sound speed of candidate liquids and narrowed the parameter space of possible core compositions.

Earlier, we discussed the use of interface temperature measurements and the inference of melting points from such observations. This type of measurement has been critical in establishing the phase diagram of Fe and hence the principal constraint on the temperature structure of the Earth's core and deep interior. However, it should be noted that for a number of metals – for example, Fe, V, Mo, and Ta (Luo and Ahrens, 2004; Luo and Swift, 2007) – the melting curves inferred from the interface shock temperature measurements (Ahrens et al., 2002; Williams et al., 1991; Yoo et al., 1993) are in stark disagreement with static high-pressure determinations (Boehler, 2000; Errandonea, 2005; Errandonea et al., 2003).

The Fe phase diagram appears to be approaching consensus among a subset of shock interface temperature determinations (Ahrens et al., 2002; Chen and Ahrens, 1998; Nguyen and Holmes, 2004), molecular dynamic models (Aitta, 2006; Alfè, 2009, 2010; Belonoshko et al., 2009), and a variety of melting criteria applied to static high-pressure experiments (Jackson et al., 2013; Morard et al., 2011; Murphy et al., 2011). For other metals, for example, Mo and Ta, there is still no clear consensus despite a number of molecular dynamics calculations (Cao et al., 2012; Liu et al., 2008; Luo and Swift, 2007) that generally favor the shock temperature-based melting curves. Possible paths to reconciling these studies include unknown phase changes or experimental errors in either static or dynamic techniques (or both).

2.16.3.5 Liquids

Dynamic compression is especially attractive in the study of liquid and other amorphous materials where techniques based

on diffraction are unavailable and many methods for measuring elasticity are challenging. Liquids are important in geophysics in several contexts, including natural waters, magma, and planetary cores. Shock experiments can probe liquid states beginning with solid materials and driving them to states that melt either upon shock or upon release. Alternatively, some materials can be melted before shocking, which simplifies the interpretation of the data by removing ambiguity about the observed phase and the need to know or estimate the transition energy associated with melting. The study of silicate liquids using preheated compression was pioneered by Ahrens, Stolper, and their students (Chen et al., 2002; Miller et al., 1991; Rigden et al., 1984, 1988, 1989), reaching pressures up to ~40 GPa. This effort continues at present, now reaching pressures up to ~150 GPa and so covering the whole pressure range of the terrestrial mantle (Asimow and Ahrens, 2010; Thomas et al., 2012). Compositions studied include diopside, $\text{CaMg}_2\text{SiO}_6$ (Asimow and Ahrens, 2010; Rigden et al., 1989); anorthite, $\text{CaAl}_2\text{Si}_2\text{O}_8$ (Asimow and Ahrens, 2010; Rigden et al., 1989); the Fe-free basalt analog diopside–anorthite eutectic (64 mol% diopside and 36 mol% anorthite) (Asimow and Ahrens, 2010; Rigden et al., 1984, 1988), komatiite (Miller et al., 1991); mid-ocean ridge basalt (Rowan, 1993); fayalite, Fe_2SiO_4 (Chen et al., 2002; Thomas et al., 2012); hedenbergite, $\text{CaFeSi}_2\text{O}_6$, and binary and ternary compositions in the diopside–anorthite–hedenbergite system (Thomas and Asimow, 2013b); and forsterite, Mg_2SiO_4 (Thomas and Asimow, 2013a). In all cases, the initial density of the liquid is not directly observed in these experiments, since the sample is heated in a sealed Mo capsule; rather, initial density at the preheat temperature (ranging from 1573 K for fayalite to 2273 K for forsterite) is obtained from partial molar volumes of the oxides estimated from inversion of Archimedeian double plumb-bob data of Lange and Carmichael (1987) or, more recently, Lange (1997).

In general, shock compression studies of preheated liquids yield simple linear Hugoniot in $U_s - u_p$ space. The intercepts C_0 (see eqn [4] in the preceding text) of unconstrained fits are normally within error of the relaxed (i.e., low frequency) bulk sound speed in the same liquid at the preheat temperature as measured by ultrasonic methods (Ai and Lange, 2008; Kress and Carmichael, 1991; Rivers and Carmichael, 1987). This suggests that, despite the very rapid compression involved in passage of a shock, the high-pressure state represents relaxed or equilibrium compression, suitable for treatment of liquid rather than glassy behavior. The issue of relaxation is addressed in general by Rigden et al. (1988) but requires independent verification, where possible, for each composition studied. Furthermore, the observations of simple linear Hugoniot that project back to ultrasonically measured sound speeds at zero strain are consistent with smooth compression behavior, without phase changes or obvious regions of enhanced coordination change or topological transitions. The shock data therefore constrain the pressure derivative of the bulk modulus, K'_S , and, in some cases, higher-order derivatives such as K''_S . An early study of diopside–anorthite eutectic liquid that extended up to 34 GPa inferred a sudden stiffening or change in compression behavior at ~24 GPa, which was interpreted as the exhaustion of topological compression mechanisms and the onset of solid-like compression behavior requiring bond

shortening (Stolper and Ahrens, 1987). A sharp change in compression due to such a mechanism implies that all similar cations in the melt are similarly coordinated, such that they can all pass through a transition over a narrow range in pressure. However, extension of the Hugoniot of this composition to 128 GPa demonstrated that the inferred stiffening was not a robust feature of the larger data set. No anomalous compression intervals are evident anywhere in the mantle pressure range. This is more consistent with the contemporary microscopic view of silicate liquid structure that emerges from high-resolution nuclear magnetic resonance spectroscopy (Allwardt et al., 2005, 2007; Kelsey et al., 2009a,b; Xue et al., 1991) and ab initio molecular dynamics simulations (de Koker, 2010; de Koker et al., 2008; Stixrude and Karki, 2005; Stixrude et al., 2009), which show a broad distribution of coordination environments about cations in the melt that smoothly shifts toward higher coordination numbers with increasing pressure.

A general observation that has emerged both from dynamic compression experiments and ab initio molecular dynamics simulations is that the Grüneisen parameter γ of silicate liquids increases with compression, whereas solids of fixed structure show the opposite behavior. This was observed, though not explored in detail, for Mg_2SiO_4 liquid by Brown et al. (1987) using sound speed measurements. It was confirmed in Mg_2SiO_4 by comparison of the Hugoniot of forsterite and wadsleyite, each shocked into the melt regime (Mosenfelder et al., 2007), and in MgSiO_3 by comparison of molten shock states obtained from perovskite, enstatite, and glass starting materials (Mosenfelder et al., 2009). The same behavior is seen in Fe_2SiO_4 and in $\text{An}_{64}\text{Di}_{36}$ ($\text{An} = \text{CaAl}_2\text{Si}_2\text{O}_8$ and $\text{Di} = \text{CaMgSi}_2\text{O}_6$) from comparison of the preheated liquid Hugoniot with data from room-temperature crystalline equivalents shocked into the liquid regime (Asimow and Ahrens, 2010; Thomas et al., 2012). SiO_2 liquid shows positive thermal expansion and hence γ at elevated pressure, comparing the Hugoniot points derived from melting of fused silica and α -quartz, but fits to partial molar volumes of liquid oxide components in multicomponent silicate liquids imply zero thermal expansion of the SiO_2 component at ambient pressure. Hence, SiO_2 , like all the silicate liquids for which the comparison of ambient pressure and high-pressure γ can be made, shows increasing γ upon compression (Figure 8). In all those liquids that have been simulated by ab initio or empirical molecular dynamics, again increasing γ with decreasing volume is found to be a general property: MgSiO_3 (Stixrude and Karki, 2005), Mg_2SiO_4 (de Koker et al., 2008), SiO_2 (Karki et al., 2007), and $\text{CaAl}_2\text{Si}_2\text{O}_8$ (de Koker, 2010; Ghiorso et al., 2009; Spera et al., 2009). The understanding of this phenomenon is currently limited; it may be due to increasing coordination of cations with densification of liquid structures (Stixrude et al., 2009) or to the importance of entropic or free-volume terms in the free energy of liquids (Jing and Karato, 2011). In any case, since the Grüneisen parameter describes the temperature gradient of an isentrope, it predicts approximately the temperature structure of a convecting magma ocean. Hence, the discovery of high values of γ at high pressures in silicate liquids has led several authors to note that a whole-mantle magma ocean (Chapter 9.04) would have steeply increasing temperature, possibly steeper

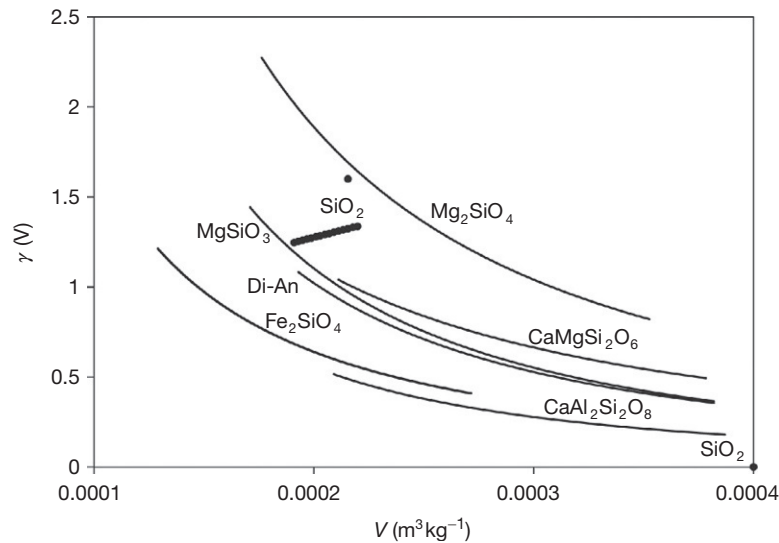


Figure 8 Estimates of the volume dependence of the thermodynamic Grüneisen parameter γ as a function of specific volume V in silicate liquids of various compositions; in all cases, data have been fit using the Mie–Grüneisen assumption that γ is a function of V only. This figure summarizes interpretations of shock wave data from Asimow and Ahrens (2010), Mosenfelder et al. (2007, 2009), and Thomas et al. (2012) and ambient-pressure properties from Ai and Lange (2008), Lange (1997), and Lange and Navrotsky (1992). In all cases, the slope of the γ – V relationship in log–log space is -1.75 ± 0.5 .

than the liquidus, and so might crystallize initially in the middle of the mantle (Labrosse et al., 2007; Mosenfelder et al., 2007, 2009; Stixrude et al., 2009; Thomas and Asimow, 2013b).

2.16.3.6 Ice and the Outer Solar System

The dynamic compression properties of ices, especially water ice – including dynamic strength, phase transitions, and melting – are important for understanding impact processes among icy bodies as well as observed features on the surfaces of cold, water-bearing terrestrial planets such as Mars. These constrain the evolution of the outer solar system, including giant planet satellites, comets, and Kuiper Belt objects. Water ice is a complicated and, in many ways, unique material. It has a negatively sloped melting curve at low pressure, a large number of solid-state phase transitions (Sanz et al., 2004), very low tensile strength, and at least two low-temperature amorphous phases (Poole et al., 1993). The dynamic failure of temperate ice was measured by Lange and Ahrens (1983, 1987), whereas the yield strength and Hugoniot properties of cold (100 K) water ice (e.g., Figure 5(b)) have been studied by Stewart–Mukhopadhyay and others (Leinhardt et al., 2008; Stewart and Ahrens, 2003, 2005; Stewart et al., 2008).

2.16.4 Future Prospects

Dynamic compression research in geophysics and planetary science, despite a history of more than 50 years of study, is in a period of rapid evolution. New technologies for extreme compression and controlled thermodynamic paths are becoming available and demonstrating their reliability. Likewise, continued progress in diagnostic technologies for wave profiles, temperature measurement, *in situ* structural determination, and

more offer opportunities to improve precision and work on smaller samples or to reduce the number of assumptions involved in interpreting results. Windows are opening for the study of geophysical materials under conditions relevant to higher pressures, motivated by the discovery of possibly Earth-like exoplanets with masses much greater than the Earth. Through expanded integration with static experiments, natural observations, and computational studies, dynamic compression will continue to be an important component of geophysical research (Chapter 2.01).

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2.17 Seismic Properties of Rocks and Minerals, and the Structure of Earth

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2.17.1 Introduction

The theoretical problem of computing the radial structure of a hydrostatic, gravitationally self-compressed body such as Earth is well developed. In its simplest form, one solves the Poisson equation together with a constitutive relation for the variation of pressure and density with depth. While such solutions are important for our understanding of the structure of stars and planets, including exo-planets (Valencia et al., 2006), they have not played a major role in our understanding of Earth's structure for at least two important reasons. The first of them is the still overwhelming complexity of the constitutive relation in the case of Earth and the other terrestrial planets. There are at least six essential elements and they are distributed inhomogeneously with depth, most evidently in the separation between the crust, mantle, and core. Moreover, there are more than ten essential phases in the mantle alone, as compared with the single fluid phase that suffices in the case of the gas giants. The second reason is the power of seismological observations to reveal Earth's structure. Adams and Williamson were able to estimate the radial density profile of Earth's mantle from a very different starting point, the observed variation of seismic wave velocities with depth, as embodied in their famous equation. The number and quality of seismic observations continues to grow as does our ability to interpret them, so that over the last few decades, seismologists have been able to constrain not only radial, but also lateral, variations in seismic wave velocities and to produce three-dimensional models of Earth's structure.

One of the goals of geophysics is to relate the structure of Earth's interior as revealed primarily by seismology, to its thermal and chemical state, its dynamics and evolution. It is not generally possible to construct this more complete picture from knowledge of the seismologically revealed structure alone. The limitations are not so much practical – there is every indication that our knowledge of Earth's structure will continue to improve for some time with further observation – as fundamental. The relationship of seismic wave velocity to composition and temperature cannot be inverted uniquely without further information.

Our primary interest in the seismic properties of Earth materials derives from this overarching goal, to place the current structural snapshot provided by seismology in the larger context of Earth's evolution. Knowledge of material properties and behavior is the essential link between seismological observations and the temperature and composition of the interior. Indeed, the combination of geophysical observation and knowledge of material properties derived from experimental and theoretical studies provides our most important constraints on the composition of the mantle and its thermal structure.

It is the aim of this chapter to illustrate the role of mineral physics as the interpretive link between seismic structure and dynamics, and to review what studies of material properties have taught us about the dynamics and composition of Earth. Our focus is on Earth's mantle because the problem of determining the chemical and thermal state is particularly rich and because substantial progress has been made in the last decade.

The organization takes its cue from Earth's seismic structure. We begin with a review of the one-dimensional elastic structure that accounts for most of the observed seismic signals. Special topics here include the origin of high gradient zones and the origin of discontinuities. We continue with a discussion of lateral variations in seismic structure and their interpretation in terms of lateral variations in temperature, composition, and phase. A discussion of anisotropy highlights the many important advances that have been made, particularly in our knowledge of the full elastic constant tensor of minerals, and also the formidable difficulties remaining, including a need for a better understanding of deformation mechanisms. We end with that part of Earth's seismic structure that is currently least amenable to interpretation, the anelastic part, indicating important developments in our understanding of the relevant material properties, and the gaps that remain in our knowledge.

2.17.2 Radial Structure

2.17.2.1 Overview

Perhaps the most remarkable and informative feature of Earth's radial structure is that it is not smooth (Table 1). The variation of seismic wave velocities with depth is broken up at several depths by rapid changes in physical properties. They are generally referred to as discontinuities, although in all probability, they represent regions where physical properties change very rapidly over a finite depth interval. Each discontinuity is associated with a mean depth, a range of depth resulting from topography on the discontinuity and a contrast in physical properties, such as

$$\frac{\Delta I}{I} = \frac{\Delta \rho}{\rho} + \frac{\Delta V}{V} \quad [1]$$

where ρ is the density and V is either the shear or longitudinal wave velocity, and Δ represents the difference across the

discontinuity. For isochemical changes in physical properties that follow Birch's law (Anderson et al., 1968), the velocity contrast is approximately two-third of the impedance contrast for S-waves and approximately three-fourth for P-waves. Of the discontinuities reported, some (e.g., 410, 660) are much more certain than others (e.g., 1200, 1700), in terms of both their existence and properties.

Discontinuities are important because they tie seismological observations to Earth's thermal and chemical state in an unusually precise and rich way. Many discontinuities in the mantle occur at depths that correspond closely to the pressure of phase transformations that are known from experiments to occur in plausible mantle bulk compositions (Figure 1). The pressure at which the phase transformation occurs depends on temperature via the Clausius–Clapeyron equation, which must be suitably generalized for multi-component transitions. The mean depth of a discontinuity then anchors the geotherm. Lateral variations in the depth of the discontinuity constrain lateral variations in temperature.

Phase transformations also influence mantle dynamics. For example, in a subducting slab, the perovskite forming reaction is delayed as compared with the surroundings, tending to impede the slab's descent. The extent to which a phase transformation alters dynamics scales with the phase buoyancy parameter (Christensen and Yuen, 1985)

$$\Phi = \frac{\gamma \Delta \rho}{g \alpha \rho^2 h} \quad [2]$$

where γ is the Clapeyron slope, g is the acceleration caused by gravity, α is the thermal expansivity, and h is the depth of the mantle. Phase transformations with negative Clapeyron slopes, such as the perovskite-forming reaction, tend to impede radial mass transfer, while those with positive Clapeyron slopes, such as the olivine to wadsleyite transformation, tend to encourage it. In the application to Earth's mantle, the phase buoyancy

Table 1 Mantle discontinuities

Discontinuity	Depth (km)	Contrast	Affinity	Ref.	Origin	Ref.
Hales	59 (12)	+7.0%	Global?	Revenaugh and Jordan (1991a)	Anisotropy	Bostock (1998)
Gutenberg	77 (14)	−9.0%	Oceans	Revenaugh and Jordan (1991a)	Anisotropy	Gung et al. (2003)
Lehmann	230 (30)	+3.8%	Continents	Revenaugh and Jordan (1991a)	Anisotropy	Gung et al. (2003)
X	313 (21)	+3.3%	Subduction	Revenaugh and Jordan (1991a)	opx=hpcpx	Woodland (1998)
–	410 (22)	+8.5%	Global	Dziewonski and Anderson (1981) and Flanagan and Shearer (1998)	ol=wa	Ringwood and Major (1970)
–	520 (27)	+3.0%	Global	Flanagan and Shearer (1998) and Shearer (1990)	wa=ri	Rigden et al. (1991)
–	660–	+8%?	Subduction	Simmons and Gurrola (2000)	ak=pv	Hirose (2002)
–	660 (38)	+15.8	Global	Dziewonski and Anderson (1981) and Flanagan and Shearer (1998)	ri=pv+mw	Ito and Takahashi (1989)
–	720 (24)	+2.0	Global?	Revenaugh and Jordan (1991a)	gt=pv	Stixrude (1997)
–	900 (150)	?	Subduction?	Kawakatsu and Niu (1994)	Comp.?	Kawakatsu and Niu (1994)
–	1200	?	Global?	Vinnik et al. (2001)	st=hy?	Karki et al. (1997b)
–	1700	?	?	Vinnik et al. (2001)	capvc=capvt?	Stixrude et al. (1996)
D''	2640 (100)	+2.0%	Fast	Lay et al. (1998a)	pv=ppv	Oganov and Ono (2004)
ULVZ	2870 (20)	−10%	Slow	Garnero and Helmberger (1996)	Melt	Williams and Garnero (1996)

Notes: Contrast is the S-wave impedance contrast, except for the D'' and ULVZ discontinuities (2640, 2870 km), which are reported as the S-wave velocity contrast. Value in parentheses following depth is the peak-to-peak (410, 520, 660), or RMS (others) variation in the depth. The estimated impedance contrast at 660– is half of that of the 660 itself, based on subequal reflectivity from 660– and 660 in the study of Simmons and Gurrola (2000). Affinity designations fast and slow refer to regions of anomalously high and low wave speeds in tomographic models, respectively. Origin designation 'comp.' refers to a contrast in bulk composition possibly associated with subducted crust. Abbreviations capvc and capvt refer to the cubic and tetragonal phases of CaSiO₃ perovskite, respectively. Entries with a question mark are either unknown or uncertain.

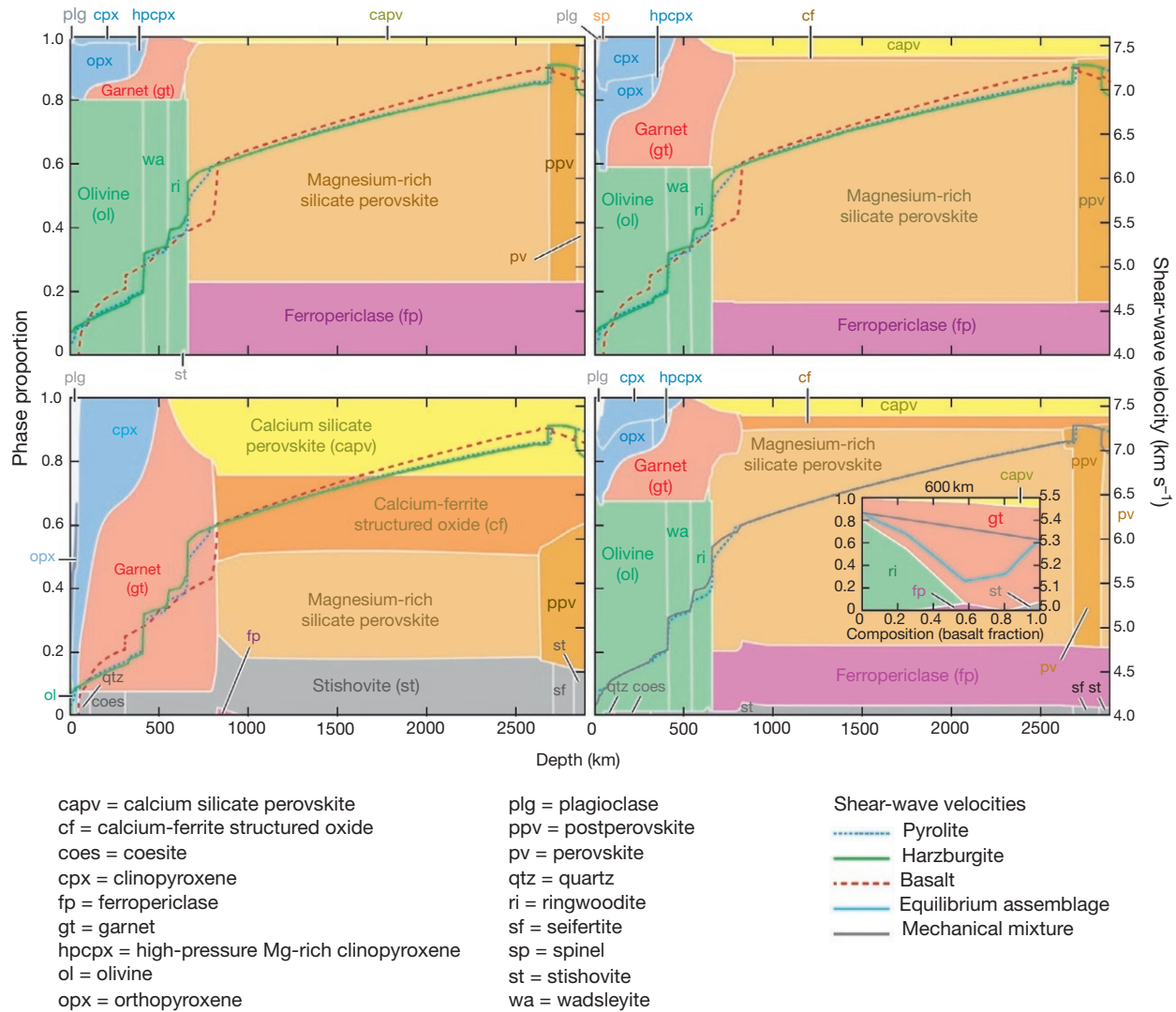


Figure 1 Phase proportions (atomic fraction) of (counterclockwise, from top right) pyrolite, harzburgite, basalt, and a mechanical mixture of 18% basalt and 82% harzburgite equal in overall bulk composition to pyrolite. Superimposed are the shear-wave velocities of pyrolite (dotted blue line), harzburgite (solid green line), basalt (dashed red line), and the mechanical mixture (solid gray line). Curves are repeated in multiple panels to permit direct comparison. Inset in the lower right panel shows the origin of the faster velocity in the mechanical mixture. Phase proportions and velocity vary with composition in an equilibrium assemblage (solid light blue line) and a mechanical mixture of the end-member compositions (solid gray line). Computed with HeFESTo (Stixrude and Lithgow-Bertelloni, 2011). All bulk compositions are taken from Xu et al. (2008). Reproduced from Stixrude L and Lithgow-Bertelloni C (2012) Geophysics of chemical heterogeneity in the mantle. *Annual Review of Earth and Planetary Sciences* 40: 569–595.

parameter must be generalized to account for the fact that only a fraction of the mantle undergoes the phase transformation (i.e., 50–60% in the case of the olivine to wadsleyite transition), and that nearly all phase transformations are at least divariant and occur over a finite range of depth.

Phase transformations also depend sensitively on bulk composition, which means that the Earth's discontinuity structure also constrains mantle chemistry. For example, the sequence of phase transformations with increasing pressure in olivine would be quite different if the mantle had twice as much FeO and would no longer resemble Earth's radial structure (Akaogi et al., 1989).

Not all discontinuities can be explained by phase transformations. In some cases, no phase transformations occur near the appropriate depth. In others, phase transformations do

occur, but the change in physical properties caused by the transition is far too subtle to explain the seismic signal. In the case of the D'' discontinuity, a phase transformation was only recently found that finally appears to explain most of the properties of this previously enigmatic structure. Rapid variation with depth in chemical composition (e.g., the Moho), the pattern or strength of anisotropy, or in the magnitude of attenuation and dispersion may also cause discontinuities.

2.17.2.2 Upper Mantle

We take the upper mantle to be that region of Earth between the Mohorovicic discontinuity and the 410-km discontinuity. This part of Earth is challenging from a mineral physics point of view because heterogeneity, anisotropy, and attenuation are

all large. Discussions of globally average radial structure are prone to mislead, which is why regional one-dimensional profiles as well as three-dimensional tomographic models are important to keep in mind. This part of Earth is remarkably rich in structure, with features that have resisted explanation in terms of mineralogical models.

One of the most remarkable features of upper mantle structure is the presence of a low-velocity zone (Gutenberg, 1959). A pattern of decreasing velocity with increasing depth appears unique to the boundary layers of the mantle (see also discussion of D'' later). The low-velocity zone is more prominent under oceans than under continents, and under young oceanic lithosphere than old (Anderson, 1989).

The origin of the low-velocity zone is readily understood in terms of Earth's thermal state and the properties of minerals. Negative velocity gradients appear whenever the thermal gradient exceeds a critical value such that the increase in velocity with compression is overcome by the decrease in velocity on heating (Anderson et al., 1968; Birch, 1969). The critical thermal gradient

$$\beta_s = -\left(\frac{\partial V_s}{\partial P}\right)_T / \left(\frac{\partial V_s}{\partial T}\right)_P \quad [3]$$

for shear waves is modest: 2 K km^{-1} for olivine. One then expects negative velocity gradients to be widespread in the shallow upper mantle, on the basis of heat flow observations. There is a critical thermal gradient for the density as well:

$$\beta_p = \frac{1}{\alpha K_T} \quad [4]$$

where α is the thermal expansivity and K_T is the isothermal bulk modulus, which is just the inverse of the thermal pressure gradient that has been discussed by Anderson (1995). The value for olivine, $\sim 10 \text{ K km}^{-1}$, is less than that in most of the Earth's upper thermal boundary layer. The low-velocity zone should be associated with locally unstable stratification in which more dense material overlies less dense material.

Comparison to the critical thermal gradient also explains much of the lateral variations in the structure of the low-velocity zone. In the half-space cooling model of the mantle, the geothermal gradient decreases with lithospheric age, producing a weaker negative velocity gradient, as seen seismologically (Graves and Helmberger, 1988; Nataf et al., 1986; Nishimura and Forsyth, 1989). Under continents, the geothermal gradient is much less steep, but even under cratons exceeds the critical value; for example, the gradient is 4 K km^{-1} under the Abitibi province (Jaupart and Mareschal, 1999). Indeed, the low-velocity zone appears to be present, although less prominently, under the continents (Grand and Helmberger, 1984; Romanowicz, 2009).

Are other factors required to quantitatively explain the values of the lowest velocities seen in the low-velocity zone? It has long been suggested that partial melt may be present in this region of the mantle (Anderson and Sammis, 1969; Birch, 1969; Green and Liebermann, 1976; Kawakatsu et al., 2009; Lambert and Wyllie, 1968; Ringwood, 1969; Sato et al., 1989). While partial melt is not required to explain the existence of a low-velocity zone per se as the argument regarding the critical thermal gradient presented earlier demonstrates, it is difficult to rule out its presence on the basis of quantitative comparisons of seismological observations to the

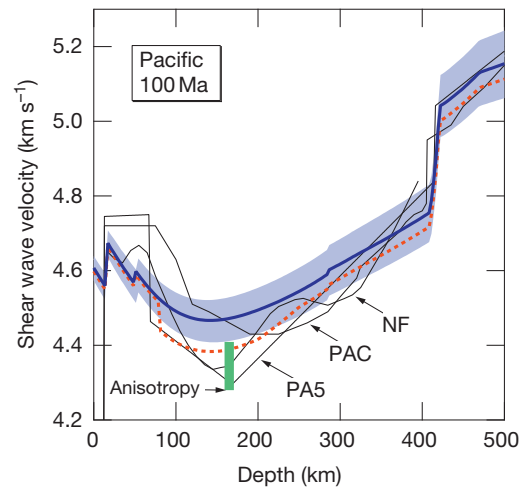


Figure 2 The shear-wave velocity of pyrolite along a 100-Ma conductive cooling geotherm in the elastic limit (bold line), and including the effects of dispersion according to the seismological attenuation model QR19 (Romanowicz, 1998) and $\alpha = 0.25$ (bold dashed). The shading represents the uncertainty in the calculated velocity. The mineralogical model is compared with seismological models (light lines) PAC (Graves and Helmberger, 1988), NF110+ (Nishimura and Forsyth, 1989), and PA5 (Gaherty et al., 1999a). The approximate magnitude of SH-SV anisotropy is indicated by the vertical bar. Reproduced from Stixrude L and Lithgow-Bertelloni C (2005) Mineralogy and elasticity of the oceanic upper mantle: Origin of the low-velocity zone. *Journal of Geophysical Research: Solid Earth* 110: B03204.

elastic properties of upper mantle assemblages. Some recent studies have concluded that partial melt is not required to explain the seismological observations, except in the immediate vicinity of the ridge (Faul and Jackson, 2005; Stixrude and Lithgow-Bertelloni, 2005b; Figure 2). These studies also find it essential to account for the effects of attenuation and dispersion, which are unusually large in this region (see later). In order for partial melt to be a viable explanation of seismic observations, melt must be thermodynamically stable at the pressure-temperature conditions of the low-velocity zone. In fact, the temperature expected in the low-velocity zone lies well below the dry solidus, and phase equilibrium calculations show that less than 0.1% of volatile-enriched partial melt is expected to be stable at the pressure-temperature conditions of most of the low-velocity zone, with the stable fraction exceeding 0.3% only near the ridge (lithospheric age $< 20 \text{ Ma}$) for plausible potential temperature and volatile content of the MORB source (Hirschmann, 2010). Another difficulty faced by the partial melt explanation is that partial melt, once produced, tends to leave the low velocity zone because it is buoyant (Stolper et al., 1981). Whether small amounts of partial melt can remain in the low-velocity zone for geologically significant periods of time is still uncertain (Hirschmann, 2010).

The low-velocity zone has sometimes been seen as being bounded above by the Gutenberg (G) discontinuity near a 65-km depth. The impedance contrast is variable, large, and negative, that is, velocities are less below the transition (Gaherty et al., 1999a; Revenaugh and Jordan, 1991a). Phase transformations occurring near this depth do not produce

velocity discontinuities of nearly sufficient magnitude, or even the right sign. A rapid change in attenuation with increasing depth produces a velocity change of the right sign (Karato and Jung, 1998), but it is far too small in magnitude (Stixrude and Lithgow-Bertelloni, 2005b). A rapid change in the partial melt fraction, from a melt-free lithosphere to a partially molten low-velocity zone, also produces a velocity change that is too small, as modeling indicates that the discontinuity is made up equally of anomalously high velocity above the discontinuity and anomalously low velocity below (Stixrude and Lithgow-Bertelloni, 2005b; Figure 2). Moreover, it is not clear that sufficient amounts of partial melt are thermodynamically stable at the pressure–temperature conditions expected at this boundary (Hirschmann, 2010). A discontinuity at a similar depth has also been associated with the lithosphere–asthenosphere boundary (Fischer et al., 2010).

The Lehmann discontinuity near a 200-km depth also does not have a counterpart in mantle phase transformations. In some global models (Dziewonski and Anderson, 1981), this discontinuity is enormous, exceeding in magnitude the much more widely studied 410-km discontinuity. The Lehmann discontinuity is observed preferentially under continents (Gu et al., 2001), while the G discontinuity is found preferentially under oceans (Revenaugh and Jordan, 1991a). It has been proposed that the Lehmann discontinuity represents a change in anisotropy caused by a change in the dominant deformation mechanism from dislocation-dominated to diffusion-dominated creep (Karato, 1992).

The Lehmann and Gutenberg discontinuities may actually be the same feature, occurring at shallower depths under oceans and greater depths under continents. Both may be caused by a change in anisotropy via a change in the pattern of preferred orientation associated with the base of the lithosphere and a transition to a more deformable asthenosphere where preferred orientation is more likely to develop (Gung et al., 2003; Romanowicz, 2009; Figure 3). This model is in apparent disagreement with those based on ScS reverberation, which require an increase in SV with increasing depth across the Lehmann discontinuity (Gaherty and Jordan, 1995; Revenaugh and Jordan, 1991a).

A smaller discontinuity called the X discontinuity is seen locally near a 300-km depth (Deuss and Woodhouse, 2002; Revenaugh and Jordan, 1991a). A phase transition appears to

be the most likely explanation (Woodland, 1998), involving a subtle modification of the orthopyroxene structure to a slightly denser monoclinic form with the same space group as diopside (clinopyroxene) (Angel et al., 1992; Jacobsen et al., 2010; Pacalo and Gasparik, 1990), or resulting from the transformation of coesite to stishovite (Williams and Revenaugh, 2005; Figure 1). The elastic properties of this unquenchable high-pressure pyroxene phase have only recently been measured and appear to confirm the connection to the seismic discontinuity (Kung et al., 2005). The velocity contrast in the pure composition is 8%, reduced to less than 0.5% in a typical pyrolite composition along a normal mantle geotherm (Stixrude and Lithgow-Bertelloni, 2005b). The proportion of orthopyroxene and, thus, the magnitude of the velocity change should increase with decreasing temperature and with depletion; indeed, the X discontinuity is preferentially observed near subduction zones.

The velocity gradient between the low-velocity zone and the 410-km discontinuity is very large (Figure 2). In some regional models, the gradient exceeds that of the transition zone (Gaherty et al., 1999a; Graves and Helmberger, 1988; Nishimura and Forsyth, 1989). According to the usual Bullen analysis, this means that this region is either non-adiabatic, or inhomogeneous in bulk composition or phase (Stixrude and Lithgow-Bertelloni, 2005b). By comparing mineral physics models directly with seismic observables, a recent study showed that the high-gradient zone can be explained by an increase in depth of the proportion of basaltic lithology (Cammarano et al., 2009).

2.17.2.3 Transition Zone

This region is so named because of the phase transformations that were anticipated and subsequently found to take place within it. While phase transformations are not restricted to the transition zone as our discussion of the upper and lower mantles makes clear, the two largest ones in terms of changes in physical properties do occur here. This region encompasses the transformation of the mantle from structures characterized by silicon in fourfold coordination in the upper mantle to those characterized by silicon in sixfold coordination in the lower mantle.

The two largest discontinuities in the mantle occur at 410- and 660-km depths. They have been explained by phase

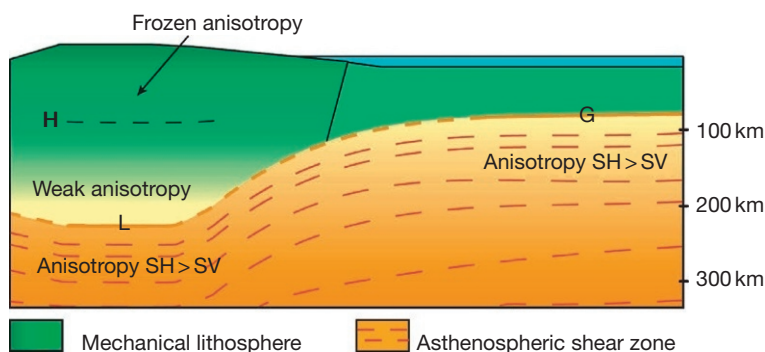
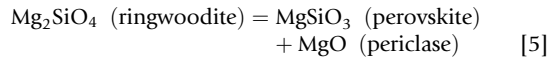


Figure 3 Sketch illustrating the pattern of anisotropy found in a recent tomographic model in relation to lithospheric thickness, and to the Lehmann (L) and Gutenberg (G) discontinuities. The Hales discontinuity (H) is also indicated. Reproduced from Gung YC, Panning M, and Romanowicz B (2003) Global anisotropy and the thickness of continents. *Nature* 422: 707–711.

transformations from olivine to its high-pressure polymorph wadsleyite for the 410 (Ringwood and Major, 1970) and from ringwoodite, the next highest pressure olivine polymorph, to the assemblage perovskite plus periclase for the 660 according to the reaction (Liu, 1976) (Figure 1)



These explanations have received considerable scrutiny over the last several years and have held up well. In addition to the issues discussed in more detail later, there has been vigorous debate concerning the pressure at which the two transformations occur and whether these, in fact, match the depth of the discontinuities (Chudinovskikh and Boehler, 2001; Fei et al., 2004; Irifune et al., 1998; Shim et al., 2001), and whether the Clapeyron slope of the transitions can account for the seismologically observed topography on the discontinuities (Helffrich, 2000).

In the case of the 410-km discontinuity, the magnitude and the sharpness of the velocity jump have also been the subject of considerable debate. Several studies have argued that the magnitude of the velocity change at the olivine to wadsleyite transition in a typical pyrolitic mantle composition is too large and that the mantle at this depth must have a relatively olivine-poor bulk composition (Duffy et al., 1995; Gwanmesia et al., 1990; Li et al., 1998; Liu et al., 2005; Zha et al., 1997). Phase equilibrium studies (Akaogi et al., 1989; Katsura and Ito, 1989) have shown that the olivine to wadsleyite transition in the binary $\text{Mg}_2\text{SiO}_4\text{--Fe}_2\text{SiO}_4$ system occurs over a depth range too wide to account for the observed reflectivity of this transition, at frequencies as high as 1 Hz (Benz and Vidale, 1993).

There have been several proposals to explain the apparent discrepancy in sharpness (Fujisawa, 1998; Ji et al., 2004; Solomatov and Stevenson, 1994). Perhaps the simplest of them recognizes that the mantle is not a binary system: chemical exchange of olivine and wadsleyite with non-transforming phases sharpens the transition considerably (Frost, 2003; Irifune and Isshiki, 1998; Katsura et al., 2004; Stixrude, 1997; Figure 4). Non-linearities inherent in the form of coexisting loops also tend to sharpen the transition (Helffrich and Bina, 1994; Helffrich and Wood, 1996; Stixrude, 1997). Modeling of finite-frequency wave propagation shows that the form of the transition predicted by equilibrium thermodynamics and a pyrolitic bulk composition can account quantitatively for the observations (Gaherty et al., 1999b). This study and others show that observations of seismic reflectivity are consistent with the shape of the phase transitions at 410- and 660-km depths (Xu et al., 2003).

The detailed form of the 410-km discontinuity is a very sensitive probe of mantle conditions. The width of the discontinuity is found to increase with decreasing temperature (Katsura and Ito, 1989), which affects the visibility of transition (Helffrich and Bina, 1994). Phase equilibria depend strongly on iron content such that the transition is broadened with iron enrichment. Iron enrichment beyond $x_{\text{Fe}}=0.15$ at normal mantle temperatures causes the transition to become univariant (infinitely sharp in a pure olivine composition), with ringwoodite coexisting with olivine and wadsleyite (Akaogi et al., 1989; Fei et al., 1991). The transition is also sensitive to water content as wadsleyite appears to have a much higher solubility than olivine (Wood, 1995), although more recent results suggest that water partitioning between these two

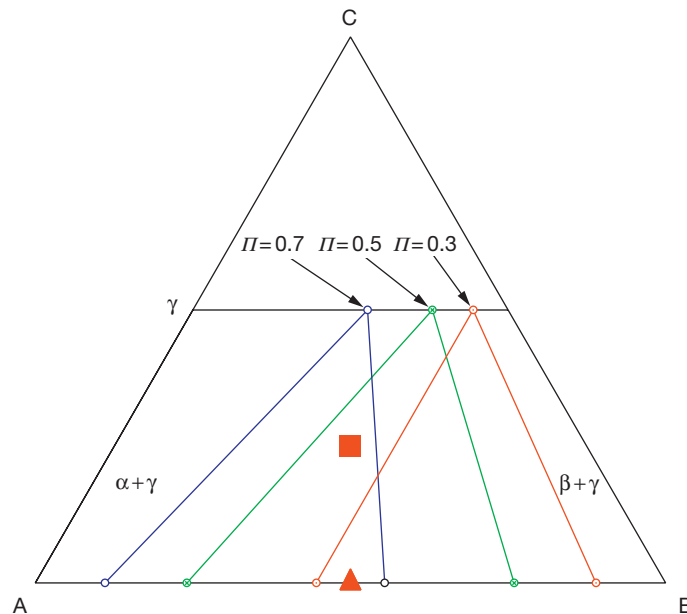


Figure 4 The influence of non-transforming phase(s) (γ) on the sharpness of the transformation from phase α to phase β . Colored lines indicate the compositions of the three coexisting phases with increasing scaled pressure (Π) within the coexistence interval. When the bulk composition lies on the A–B join, the transition is broad: the bulk composition represented by the solid triangle lies within the coexistence region over the entire pressure range shown ($\Pi=0.3\text{--}0.7$). When component C is added, the transition occurs over a narrower pressure interval: the bulk composition represented by the solid square lies within the coexistence region over a fraction of the pressure range shown ($\Pi=0.5\text{--}0.7$). Reproduced from Stixrude L (1997) Structure and sharpness of phase transitions and mantle discontinuities. *Journal of Geophysical Research: Solid Earth* 102: 14835–14852.

phases as well as the influence of water on the form of the 410 is not as large as previously assumed (Hirschmann et al., 2005). Portions of the mantle are found to have broad and non linear 410 discontinuities, consistent with the anticipated effects of water enrichment (van der Meijde et al., 2003).

In some locations, the 410 is overlain by low-velocity patches that have been interpreted as regions of partial melt, perhaps associated with water enrichment. These patches appear to be associated with present or past subduction, suggesting the slab as a possible source of water (Obayashi et al., 2006; Revenaugh and Sipkin, 1994; Song et al., 2004), although a recent global study found no correlation with surface tectonics (Tauzin et al., 2010). Other interpretations involving much more pervasive fluxing of water through the transition zone have also been advanced (Bercovici and Karato, 2003), although it has been argued that this scenario is inconsistent with the thermodynamics of water-enhanced mantle melting (Hirschmann et al., 2005). Measurements and first-principles simulations of the density of hydrous melt at the pressure of the 410 indicate that it may be gravitationally stable (Matsukage et al., 2005; Mookherjee et al., 2008; Sakamaki et al., 2006). Simulations also indicate that hydrous melt has a significantly higher electrical conductivity than anhydrous melt and that this may explain the geophysically inferred electrical conductivity anomalies atop the 410-km discontinuity (Mookherjee et al., 2008; Toffelmier and Tyburczy, 2007).

Initial studies of the influence of iron on the ringwoodite to perovskite plus periclase transition also seemed to indicate that this transition was too broad to explain reflectivity

observations (Jeanloz and Thompson, 1983; Lees et al., 1983). But in a seminal study, Ito and Takahashi (1989) showed that this transition was remarkably sharp, occurring over a pressure range less than the experimental resolution (0.1 GPa). The unusual sharpness was subsequently explained in terms of Mg–Fe partitioning and non-ideal Mg–Fe mixing in the participating phases (Fei et al., 1991; Wood, 1990). While the central result of Ito and Takahashi's study remains unchallenged, it will be important to replicate these results in realistic mantle compositions (Litasov et al., 2005; Nakajima et al., 2012), and to further explore the thermochemistry of the phases involved.

The reaction (eqn [5]) has proved to be central to our understanding of mantle petrology because it captures a fundamental difference between the upper and lower mantles. In the upper mantle and transition zone, the orthosilicate (olivine and its high-pressure polymorphs) and metasilicate (pyroxenes, garnet) systems barely interact chemically. This weak interaction is the basis for a number of petrologic studies in which the behavior of the individual systems is studied separately. Equation [5], however, represents a break, with orthosilicate (left-hand side) transforming to metasilicate.

More recent results emphasize the essential interaction of orthosilicate and metasilicate systems at temperatures just a little hotter or colder than the canonical ~ 1600 K isentrope. These interactions have important implications for the structure of the 660-km discontinuity (Figure 5). In relatively cold mantle, the transition (eqn [5]) is preceded by (Weidner and Wang, 1998)

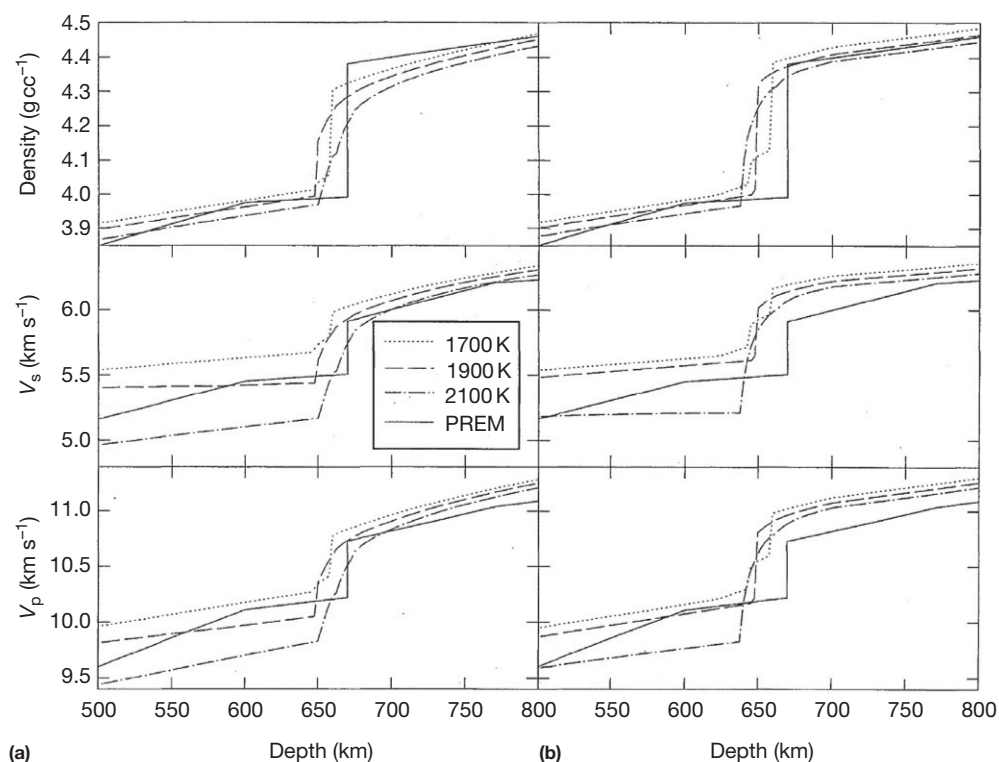
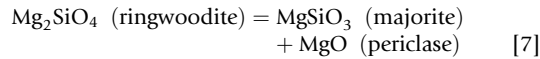


Figure 5 Calculated density and elastic-wave velocities for different geotherms for pyrolite-like compositions with (a) 3% Al_2O_3 and (b) 5% Al_2O_3 . The calculations are compared with the PREM seismological model (Dziewonski and Anderson, 1981). Reproduced from Weidner DJ and Wang YB (1998) Chemical- and Clapeyron-induced buoyancy at the 660 km discontinuity. *Journal of Geophysical Research: Solid Earth* 103: 7431–7441.



while in hot mantle, the amount of ringwoodite is diminished prior to the transition (eqn [5]) via (Hirose, 2002)



In cold and hot mantles, the reactions (eqns [5]–[7]) are followed by a further reaction:



The sequence eqns [5] and [6] produce a ‘doubled’ 660 in which a single velocity jump is replaced by two that are closely spaced in depth and of similar magnitude. There is some seismological evidence for this doubling in some locations (Deuss et al., 2006; Simmons and Gurrola, 2000; Tibi et al., 2007). The relative importance of reactions ([5]–[8]) also depends on the bulk composition, particularly the Al content (Weidner and Wang, 1998).

Below 660 is a steep velocity gradient that may be considered a continuation of the transition zone. This feature is seen in mineralogical models as the signature of the garnet to perovskite transition (eqn [8]), which is gradual and spread out over more than 100 km (Weidner and Wang, 1998). The gradual nature of this transition, as opposed to the much sharper ones discussed so far, is readily understood. The difference in composition between Al-rich garnet and relatively Al-poor perovskite is large, and this creates a broad pressure–composition coexistence region (phase loop) (Akaogi et al., 2002; Hirose et al., 2001). Although it is broad, this transition may be responsible for a seismic discontinuity seen in some studies near a 720-km depth (Deuss et al., 2006; Revenaugh and Jordan, 1991a; Stixrude, 1997). The apparent bifurcation of the 660 may then have two distinct sources: eqns [5] and [6] in cold mantle, and eqns [5] and [8] in hotter mantle. It is conceivable that three reflectors may be observable in cold mantle (eqns [5], [6], and [8]), although this has not yet been seen.

The 520-km discontinuity is seen in global stacks of SS precursors (Shearer, 1990); while there is also evidence that it is only regionally observable (Gossler and Kind, 1996; Gu et al., 1998; Revenaugh and Jordan, 1991b). Phase transformations that may contribute to this discontinuity include that of wadsleyite to ringwoodite (Rigden et al., 1991) and the exsolution of calcium perovskite from garnet (Ita and Stixrude, 1992; Koito et al., 2000). Both these transitions are broad, which may account for the intermittent visibility of the 520. Seismological evidence for doubling of this discontinuity in some regions has renewed interest in the structure and sharpness of these transitions (Deuss and Woodhouse, 2001; Saikia et al., 2008). The 520-km discontinuity has also been attributed to chemical heterogeneity, possibly associated with subduction (Sinogeikin et al., 2003).

In addition to velocity discontinuities, the transition zone is distinguished by an unusually large velocity gradient, which exceeds that of any individual transition zone phase (Figure 6). Most explanations have focused on the series of phase transformations that occur in the transition zone as the cause of this gradient. These include not only those already mentioned in

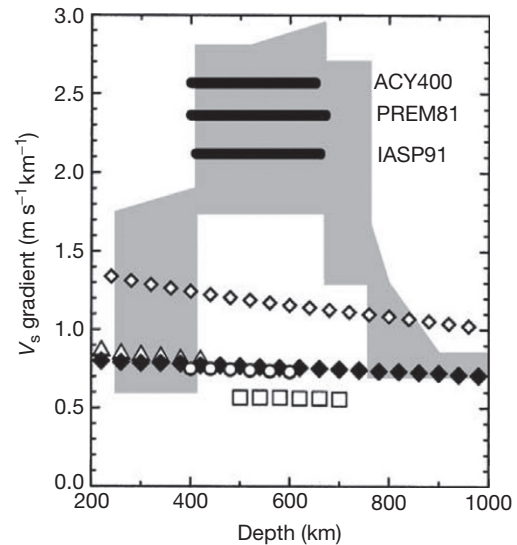


Figure 6 The velocity gradient from seismic studies and mineral physics. The shaded area is from Kennett (1993). The average gradients from global seismic models PREM81, ACY400, and IASP91 (Dziewonski and Anderson, 1981; Kennett and Engdahl, 1991; Montagner and Anderson, 1989) are shown by horizontal solid lines. Solid diamonds are extrapolation of Brillouin spectroscopy data on a garnet of 1:1 majorite:pyrope composition, and open diamonds are an extrapolation of data of Liu et al. (2000) on the same composition. Triangles – olivine, circles – wadsleyite, squares – ringwoodite. All velocity extrapolations are along a 1673 K adiabat. Reproduced from Sinogeikin SV and Bass JD (2002) Elasticity of majorite and a majorite–pyrope solid solution to high pressure: Implications for the transition zone. *Geophysical Research Letters* 29: 1017.

connection with discontinuities, but also broader features such as the dissolution of pyroxenes into garnet. The standard model – that the transition zone is adiabatic and chemically homogeneous, with a pyrolitic composition – has been tested successfully against seismological constraints on the bulk sound velocity (Ita and Stixrude, 1992). Quantitative tests against the longitudinal and shear-wave velocity are still hampered by uncertainties in the physical properties of key phases, particularly garnet–majorite (Liu et al., 2000; Sinogeikin and Bass, 2002) and CaSiO_3 perovskite. This situation has recently changed with the first measurements of the elastic wave velocities of mantle phase at mantle conditions (Irifune et al., 2008; Murakami et al., 2012). A recent study found that the velocity gradient in the transition zone is best explained by a mechanically heterogeneous mantle consisting of basalt and harzburgite, which has a higher velocity gradient than homogeneous pyrolite of the same composition (Xu et al., 2008).

2.17.2.4 Lower Mantle

The most prominent seismic anomaly in the lower mantle is the division between the D'' layer and the rest. The D'' layer is distinguished by a change in radial velocity gradient and a velocity discontinuity at its top (Lay and Helmberger, 1983). The velocity discontinuity is prominent where it is seen, although it is not present everywhere and is larger in S than

in P (Lay et al., 1998a; Wyssession et al., 1998; Young and Lay, 1987). Below this discontinuity, most models show velocity decreasing with increasing depth: the D'' represents the mantle's second low-velocity zone. In analogy to that in the shallow mantle, the D'' velocity gradient may also be caused by superadiabatic temperature gradients associated with the lower dynamical boundary layer of mantle convection.

Mineralogical explanations of the D'' discontinuity now focus on the transformation from MgSiO₃ perovskite to the post-perovskite phase (Figure 7; Murakami et al., 2004; Oganov and Ono, 2004; Tsuchiya et al., 2004a). The transition appears to occur at the right pressure and to have the right Clapeyron slope to explain the intermittent visibility. Predictions of the elastic constants show a larger contrast in V_s than in V_p , consistent with most seismological observations of the discontinuity (Iitaka et al., 2004; Tsuchiya et al., 2004b; Wentzcovitch et al., 2006; Wookey et al., 2005). Indeed, a phase transformation with very similar properties was anticipated on the basis of a combined seismological and geodynamical study (Sidorin et al., 1999). More recent studies have focused on the dependence of the depth and width of the transition on bulk composition (Catalli et al., 2009; Grocholski et al., 2012). For a pyrolite composition, the transition may not occur within the pressure regime of the mantle at all, while the transition is significantly shallower and narrower in harzburgitic and basaltic compositions (Grocholski et al., 2012). The absolute pressure of the transition as measured experimentally is still subject to considerable uncertainty arising from pressure calibration (Shim, 2008).

The ultra-low-velocity zone is a narrow intermittent layer less than 40 km thick, with shear-wave velocities approximately 10% lower than that of the rest of D'' (Garnero and Helmberger, 1996). It is still unclear what could cause such a large anomaly. A search for explanations is hampered by uncertainties concerning the relative magnitude of density and longitudinal and shear-velocity anomalies. Many studies have focused on the possibility of partial melt in this region (Stixrude and Karki, 2005; Williams and Garnero, 1996). Others have emphasized the role of iron enrichment, possibly related to chemical reaction between mantle and core (Garnero and Jeanloz, 2000; Wicks et al., 2010), or subduction (Dobson and Brodholt, 2005). In the limit of extreme iron-enrichment, the ultra-low-velocity zone may be more properly regarded as the outermost layer of the core, rather than the bottom-most layer of the mantle (Buffett et al., 2000).

There have been persistent reports of reflection or scattering from within the lower mantle (Castle and van der Hilst, 2003; Deuss and Woodhouse, 2002; Johnson, 1969; Kaneshima and Helffrich, 1998; Kawakatsu and Niu, 1994; Lestunff et al., 1995; Paulssen, 1988; van der Meijde et al., 2005; Vinnik et al., 2001). They are only locally observed, and so may be associated either with chemical heterogeneity, possibly related to subduction (Kaneshima and Helffrich, 1998; Kawakatsu and Niu, 1994), or with a phase transition that has either a weak velocity signal or a large Clapeyron slope. Phase transformations that are expected to occur in the lower mantle and that are associated with significant velocity anomalies include (Figure 8) the following: (1) Phase transformations in silica, from stishovite to CaCl₂ to α -PbO₂ structured phases (Carpenter et al., 2000; Karki and Stixrude, 1999; Karki et al.,

1997b). Free silica would be expected only in enriched compositions, such as deeply subducted oceanic crust. The first of these transitions has a particularly large elastic anomaly. (2) A phase transformation in calcium perovskite from tetragonal to cubic phases (Stixrude et al., 1996, 2007).

2.17.2.5 Core

It is known that the properties of the outer core do not match those of pure iron, which is significantly denser (Birch, 1964; Brown and McQueen, 1986). The search for the light element is still in its infancy, with the number of candidate light elements seeming to grow rather than narrow with time (Poirier, 1994). It has been pointed out that there is no a priori reason to believe that the composition of the core is simple or that it contains only one element or a few other than iron (Stevenson, 1981). In any case, further experimental and theoretical constraints on the phase diagrams and physical properties of iron light element systems will be essential to the solution.

Two relatively new approaches to constraining the nature and amount of light element in the core show considerable promise. The first relates the partitioning of candidate light elements between solid and liquid phases to the density contrast at the inner core boundary (Alf   et al., 2002a). While sulfur and silicon are found to partition only slightly, producing a density jump that is too small, oxygen strongly favors the liquid phase, producing a density jump that is too large. Within the accuracy of the theoretical calculations used to predict the partitioning, this study then appears to rule out each of these three as the sole light element in the inner core, and suggests a combination of oxygen with either silicon or sulfur as providing a match to the seismologically observed properties. Another approach is to test core formation hypotheses via experimental constraints on element partitioning between core and mantle material. In the limit that proto-core liquid approached equilibrium with the mantle as it descended, experiments point to sulfur as the only one that is sufficiently siderophile to remain in significant amounts in iron at pressures thought to be representative of core formation (~30 GPa) (Li and Agee, 1996). On the other hand, experimental simulations of the core-mantle boundary (136 GPa) show substantial reaction between core and mantle material and incorporation of large amounts of Si and O in the metal (Knittle and Jeanloz, 1989; Takafuji et al., 2005; Tsuno et al., 2013; Figure 9).

The temperature in the core is best constrained by the melting temperature of iron and iron alloys. Consensus has been building in recent years on the melting temperature of pure iron near the inner core boundary. First-principles theory (Alf   et al., 2002b), static compression (Anzellini et al., 2013; Tateno et al., 2010), and temperature measurements in dynamic compression (Nguyen and Holmes, 2004), all converge on the melting temperature proposed by Brown and McQueen (1986) on the basis of dynamic compression and modeled temperatures. The largest remaining uncertainty appears to be the influence of the light element on the melting temperature. Density functional theory predicts a freezing point depression of 700 K for light element concentrations required to match the density deficit (Alf   et al., 2002a), similar to estimates based on the van Laar equation (Brown and

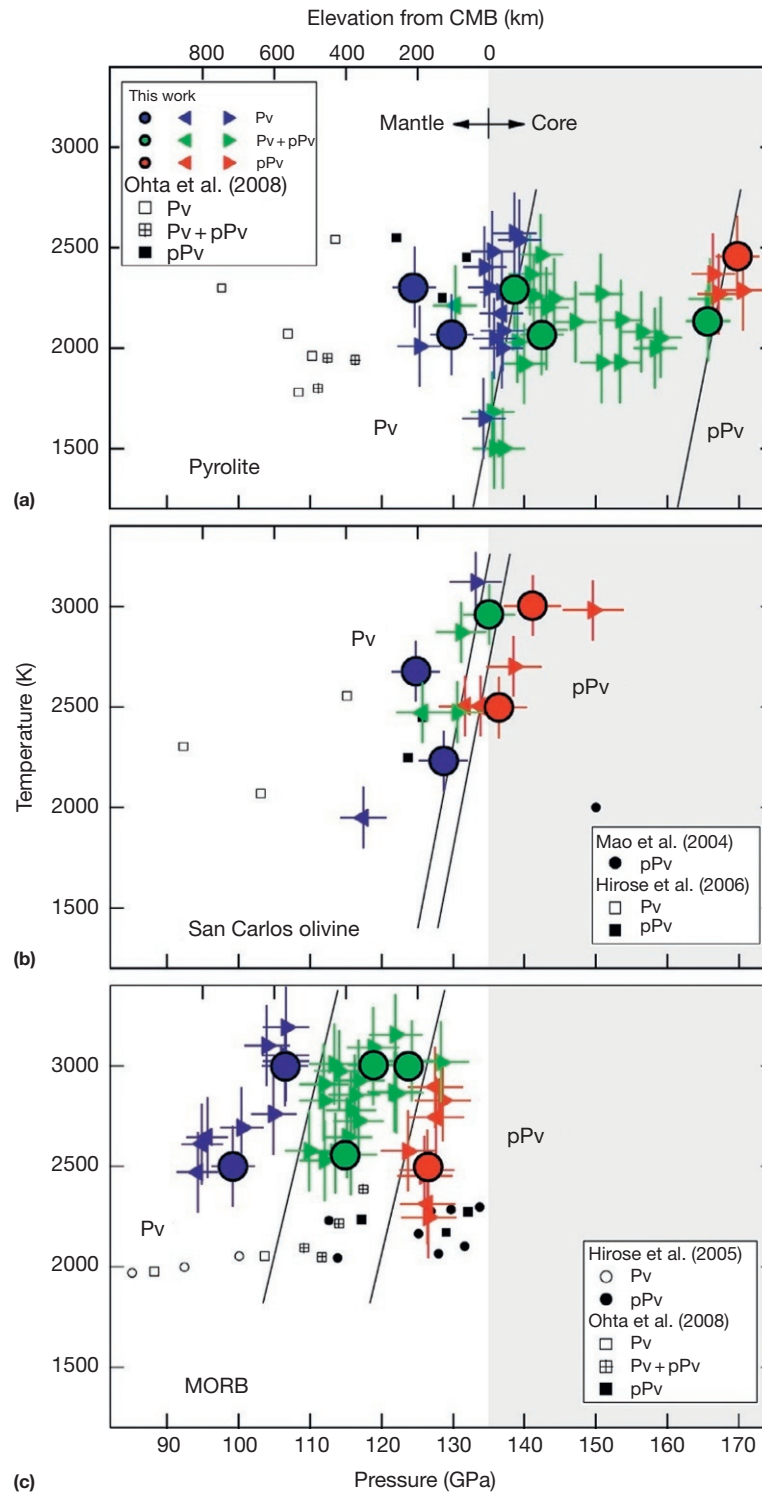


Figure 7 The pressure–temperature conditions for the stability of Pv , $Pv + pPv$, and pPv in (a) calcium-free pyrolytic, (b) San Carlos olivine, and (c) MORB compositions. The right- and left-pointing triangles represent data points measured along the forward and reverse paths, respectively, and the large circles represent the data points obtained directly from heating of amorphous starting materials. Blue, green, and red triangles represent observations of Pv , $Pv + pPv$, and pPv , respectively. The solid black lines are the phase boundaries determined from the data. The Clapeyron slope of the boundary was obtained from [Catalli et al. \(2009\)](#). The black symbols are the data points from previous studies in related compositions ([Hirose et al., 2005](#); [Mao et al., 2004](#); [Ohta et al., 2008](#)). Error bars are 1σ uncertainties. Reproduced from Grocholski B, Catalli K, Shim SH, and Prakapenka V (2012) Mineralogical effects on the detectability of the postperovskite boundary. *Proceedings of the National Academy of Sciences of the United States of America* 109: 2275–2279.

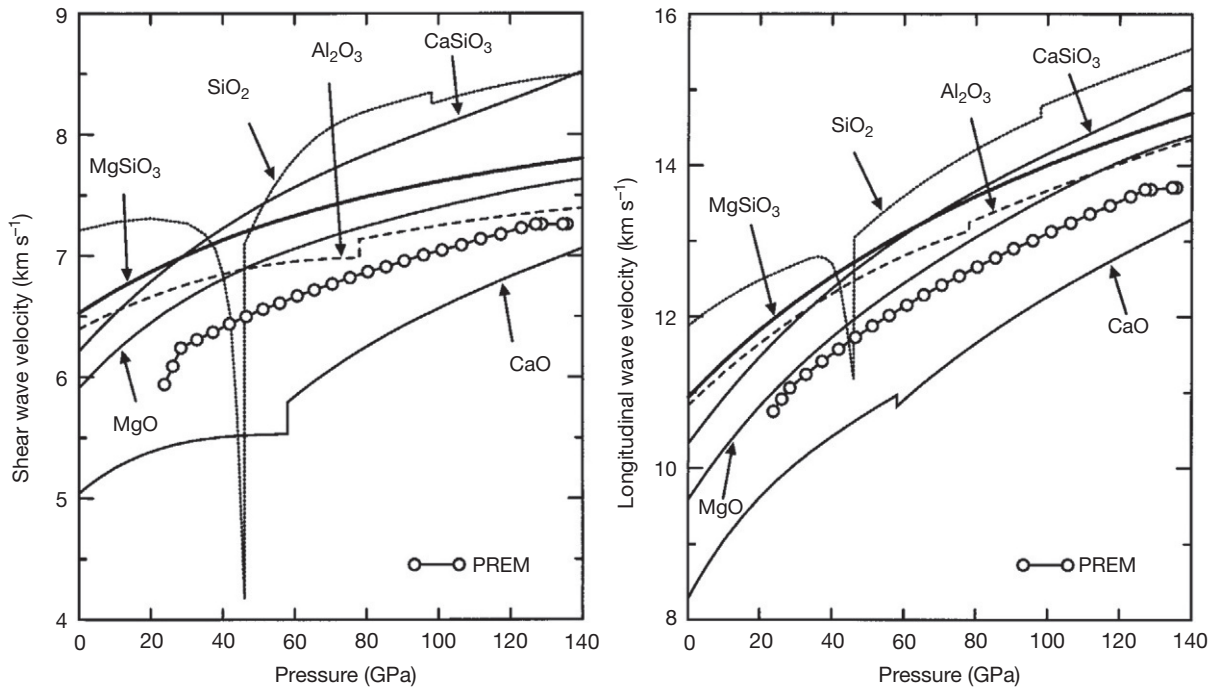


Figure 8 Comparisons of the shear- (left) and longitudinal- (right) wave velocities of lower mantle minerals computed via density functional theory at static conditions compared with the PREM model (Dziewonski and Anderson, 1981). The discontinuous changes in SiO_2 are caused by phase transformations from stishovite to the CaCl_2 structure (45 GPa) and then to the $\alpha\text{-PbO}_2$ structure (100 GPa). Reproduced from Karki BB and Stixrude L (1999) Seismic velocities of major silicate and oxide phases of the lower mantle. *Journal of Geophysical Research* 104: 13025–13033.

McQueen, 1982). An alternative approach to estimating the temperature at Earth's center is to compare the elasticity of iron to that of the inner core. This leads to an estimate of 5400 K at the inner core boundary, consistent with estimates based on melting temperatures (Steinle-Neumann et al., 2001).

The outer core is homogeneous and adiabatic to within seismic resolution (Masters, 1979) and represents possibly the clearest opportunity for estimating the temperature increment across any layer in Earth. The adiabatic temperature gradient

$$\left(\frac{\partial \ln T}{\partial P}\right)_s = \frac{\gamma}{K_s} \quad [9]$$

depends on K_s , which is known as a function of depth from seismology, and the Grüneisen parameter γ , which has been measured for pure iron (Brown and McQueen, 1986). Integrating this equation across the outer core produces a temperature difference of 1400 K, yielding a temperature of 4000 K at the core–mantle boundary (Nimmo et al., 2004; Steinle-Neumann et al., 2002). The influence of the light element on the Grüneisen parameter is not necessarily negligible and will need to be measured to test this prediction.

One of the most remarkable features of core structure is inner core anisotropy. Longitudinal waves travel a few percent faster along a near-polar axis than in the equatorial plane (Morelli et al., 1986; Woodhouse et al., 1986). Lattice-preferred orientation seems a natural explanation because all plausible crystalline phases of iron have single crystal elastic anisotropy at the relevant conditions that exceeds the elastic anisotropy of the inner core (Söderlind et al., 1996; Stixrude and Cohen, 1995), notwithstanding disagreements about the

values of the high-temperature elastic constants as predicted by different levels of ab initio theory (Gannarelli et al., 2005; Steinle-Neumann et al., 2001; Vocadlo, 2007). The identity of the stable phase is critical as the patterns of anisotropy in body-centered cubic and hexagonal candidates are very different. While the body-centered cubic phase appears to be elastically unstable for pure iron, favoring a hexagonal close-packed inner core, there is some evidence that light elements and nickel tend to stabilize this structure (Lin et al., 2002a,b; Vocadlo et al., 2003). Still unknown is the source of stress that might produce a preferred orientation, or knowledge of the dominant slip planes and critical resolved shear stresses that would permit prediction of texture, given an applied stress.

Further seismological investigations have shown that the structure of the inner core is also laterally heterogeneous (Creager, 1997; Deuss et al., 2010; Su and Dziewonski, 1995; Tanaka and Hamaguchi, 1997), and that there may be a distinct innermost layer (Ishii and Dziewonski, 2002), which may be the result of a phase transformation. Dynamical modeling studies have proposed that the approximately degree-one pattern of lateral heterogeneity can be explained by the lowest-order, degree-one convective instability of the inner core, which results in melting on one side, and freezing on the other (Alboussiere et al., 2010; Monnereau et al., 2010).

2.17.3 Lateral Heterogeneity

2.17.3.1 Overview

Lateral variations in seismic wave velocities have three sources: lateral variations in temperature, chemical composition, and

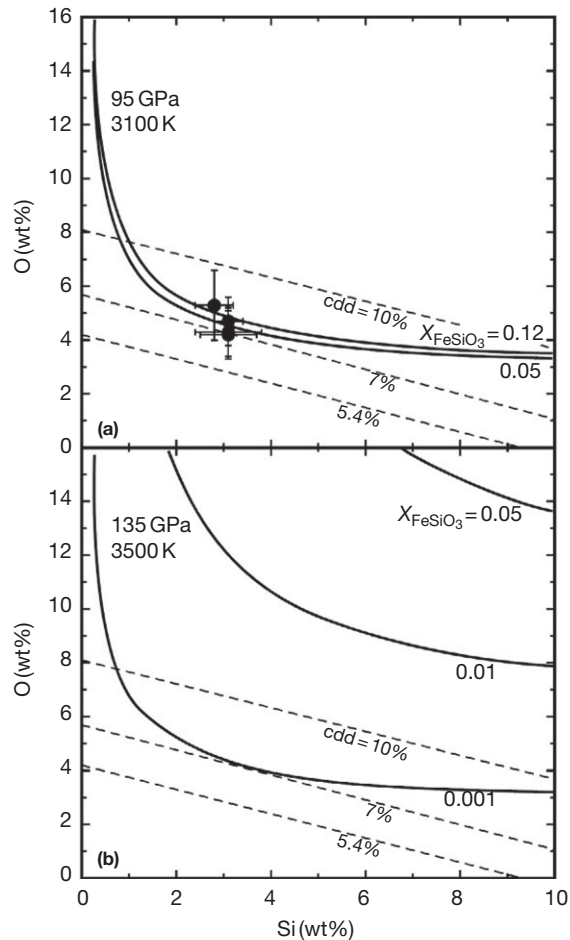


Figure 9 The simultaneous solubilities of O and Si in liquid iron in equilibrium with (Mg,Fe)SiO₃ perovskite. Solid curves represent values calculated from a thermodynamic model at (a) 95 GPa and 3100 K and (b) 135 GPa and 3500 K as a function of the FeSiO₃ component in coexisting perovskite (X_{FeSiO_3}). The model is constrained by experimental measurements, a subset of which are shown in (a) at 93–97 GPa and 3050–3150 K in contact with (Mg,Fe)SiO₃ perovskite ($X_{\text{FeSiO}_3} = 0.04 - 0.12$) (circles). The broken lines show the amounts of O and Si that are required to account for a core density deficit (cdd) relative to pure iron of 10%, 7%, and 5.4% (Anderson and Isaak, 2002). Reproduced from Takafuji N, Hirose K, Mitome M, and Bando Y (2005) Solubilities of O and Si in liquid iron in equilibrium with (Mg,Fe)SiO₃ perovskite and the light elements in the core. *Geophysical Research Letters* 32: L06313.

phase assemblage (Figure 10). The first of them has received the most attention. Indeed, comparison of tomographic models with surface tectonic features indicates that temperature may be the largest source of lateral variations: arcs are slow, cratons and subducting slabs are fast, and there is a good correlation between the history of past subduction and the location of fast velocity anomalies throughout the mantle. Quantifying these interpretations has proved challenging. One reason is that temperature is almost certainly not the only important factor. For example, it is recognized that continental mantle lithosphere must be depleted in order to remain dynamically stable, and that this depletion contributes, along with temperature, to the velocity anomaly (Jordan, 1975).

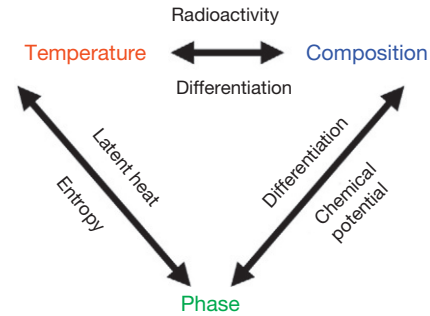


Figure 10 The three sources of lateral heterogeneity in Earth's mantle: lateral variations in temperature, in chemical composition, and phase. Arrows indicate that these three sources influence one another. Increasing temperature alters the relative stability of phases via contrasts in entropy, and may generate changes in composition via differentiation caused by partial melting. Changes in composition may include changes in the concentration of radioactive heat-producing elements and, therefore, temperature, and influence phase stability through the chemical potential. Changes in phase release or absorb latent heat, thus altering the temperature, and may produce density contrasts that lead to differentiation, potentially altering the composition.

Throughout the upper 1000 km of the mantle, lateral variations in phase assemblage may contribute as much as the influence of temperature alone. In the lower mantle, it can be demonstrated that sources other than temperature are required to explain the lateral heterogeneity.

2.17.3.2 Temperature

Several studies have sought to estimate lateral variations in temperature in the upper mantle on the basis of tomographic models and measured properties of minerals (Godey et al., 2004; Goes et al., 2000; Sobolev et al., 1996). These estimates are consistent with the results of geothermobarometry, surface tectonics, and heat flow observations. In one sense, the upper mantle is an ideal testing ground for the physical interpretation of mantle tomography because the elastic constants of the constituent minerals are relatively well known. But the upper mantle is also remarkably complex. A potentially important factor that is not accounted for in these studies is the lateral variations in phase proportions. Another source of uncertainty is anelasticity, which magnifies the temperature dependence of the velocity by an amount that is poorly constrained experimentally.

The temperature dependence of the seismic wave velocities of mantle minerals decreases rapidly with increasing pressure (Figure 11). If we ascribed a purely thermal origin to lateral structure, we would then expect the amplitude of tomographic models to decrease rapidly with depth. But tomographic models show a different pattern. The amplitude tends to decrease rapidly in the upper boundary layer, reaches a minimum at mid-mantle depths, and then increases with depth in the bottom half of the mantle. Part of the increase in amplitude with depth may be associated with the lower thermal boundary layer, where we would expect lateral temperature variations to exceed that in the mid-mantle. While concerns regarding radial resolution of tomographic models cannot be dismissed, it

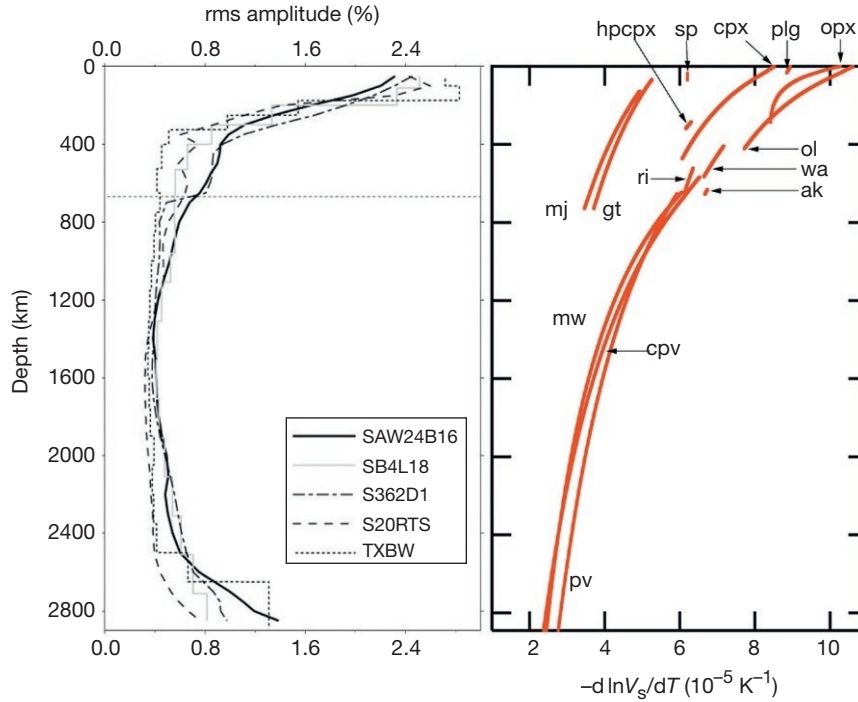


Figure 11 The amplitude of tomographic models as a function of depth (left) from Romanowicz (2003) as compared with the temperature derivative of the shear-wave velocity for mantle minerals along a typical isentrope (right) from Stixrude and Lithgow-Bertelloni (2005a).

seems likely that this aspect of lower mantle structure cannot be explained by temperature alone.

Another indication that temperature alone cannot explain lower mantle structure is the comparison of lateral variations in S and P wave velocities. The ratio

$$R = \left(\frac{\partial \ln V_S}{\partial \ln V_P} \right)_z \quad [10]$$

where V_S is the shear-wave speed and V_P is the longitudinal-wave speed, and the subscript z indicates that variations are at constant depth, reach values as large as 3.5 in the lower mantle, and appear to increase systematically with increasing depth (Bolton and Masters, 2001; Ritsema and van Heijst, 2002; Robertson and Woodhouse, 1996). This is to be compared with

$$R_{\text{thermal}} = \left[\frac{(1-A)(\delta_S - 1)}{\Gamma - 1} + A \right]^{-1} \quad [11]$$

where $A = 4/3 V_S^2 / V_P^2$, $\delta_S = (\partial \ln K_S / \partial \ln \rho)_P$, and $\Gamma = (\partial \ln G / \partial \ln \rho)_P$. The ratio takes on its limiting value $R_{\text{thermal}} \rightarrow A^{-1} \approx 2.5$ as $\delta_S \rightarrow 1$. In some portions of the mantle, lateral variations in shear and bulk sound velocities appear to be anti-correlated: regions that are slow in V_S are fast in V_B (Masters et al., 2000; Su and Dziewonski, 1997; Vasco and Johnson, 1998). Both large values of R and anti-correlated V_S and V_B require $\delta_S < 1$ if they are to be explained by temperature alone, a condition not met by lower mantle minerals. All lower mantle phases have $\delta_S > 1$ so that longitudinal, shear, and bulk sound velocities decrease with increasing temperature (Agnon and Bukowski, 1990; Karki et al., 1999; Oganov et al., 2001; Wentzcovitch et al., 2004). Anelasticity increases the value of R_{thermal} (Karato,

1993), but apparently not sufficiently to account for the tomographic value (Brodholt et al., 2007; Masters et al., 2000), and in any case, it cannot produce anti-correlation in V_S and V_B (Matas and Bukowski, 2007). The seismological determination of R is not straightforward as it relies on the comparison of different datasets (P and S travel times) with different spatial resolution and frequency content.

2.17.3.3 Composition

Of the five major cations in the mantle, iron has the largest influence on the density and the elastic wave velocities. The influence of iron content on the shear velocity differs substantially among the major mantle minerals. This means that different bulk compositions (e.g., MORB, pyrolite) will have different sensitivities to lateral variations in iron content (Speziale et al., 2005; Figure 12).

What sort of lateral variations in composition might explain the unusual features of lower mantle structure? A definitive answer is prevented by our ignorance of the elastic properties of lower mantle phases. Lateral variations in iron content do not appear capable of producing anti-correlation in bulk and shear-wave velocity, as both velocities are decreased by addition of iron to MgSiO_3 perovskite (Kiefer et al., 2002). It has been argued that lateral variations in Ca content can produce anti-correlation because CaSiO_3 perovskite has a greater shear-wave velocity but a lesser bulk sound velocity than MgSiO_3 perovskite (Karato and Karki, 2001). However, this argument is based on first-principles calculations of CaSiO_3 perovskite that assumed a cubic structure (Karki and Crain, 1998). One of the remarkable features of this phase is that it undergoes a slight non cubic distortion with decreasing

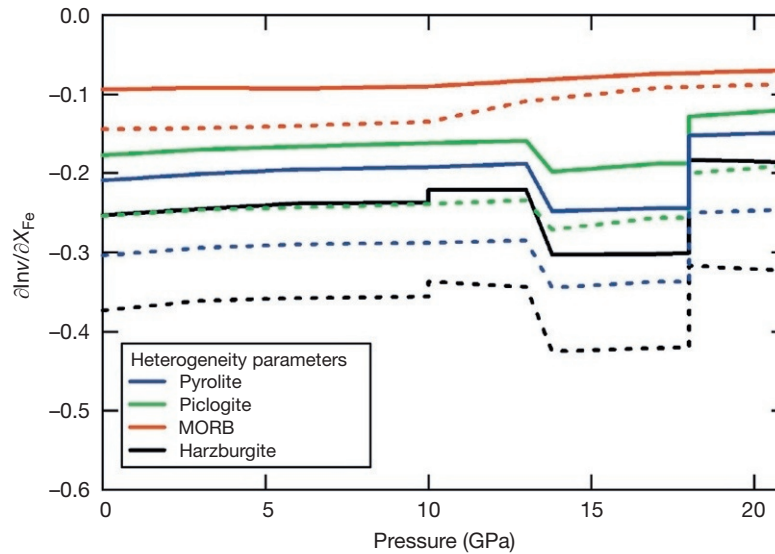


Figure 12 Sensitivity of compressional and shear-wave velocity heterogeneity parameters to Fe–Mg substitution calculated for pyrolite, piclogite, harzburgite, and MORB, along an isentropic pressure/temperature path with a potential temperature of 1673 K. Solid lines: $\partial \ln v_p / \partial X_{Fe}$, dashed lines: $\partial \ln v_s / \partial X_{Fe}$. Reproduced from Speziale S, Jiang F, and Duffy TS (2005) Compositional dependence of the elastic wave velocities of mantle minerals: Implications for seismic properties of mantle rocks. In: van der Hilst RD, et al. (eds.) *Earth's Deep Mantle: Structure, Composition, and Evolution*, pp. 301–320. Washington, DC: American Geophysical Union.

temperature (Adams and Oganov, 2006; Ono et al., 2004; Shim et al., 2002; Stixrude et al., 1996) that nevertheless produces a very large 15% softening of V_s , while leaving the density and V_p virtually unaffected (Stixrude et al., 2007).

Dynamical models suggest that lateral variations in composition in the lower mantle may be associated with segregation of basalt (Christensen and Hofmann, 1994; Davies, 2006; Nakagawa and Buffett, 2005; Stixrude and Lithgow-Bertelloni, 2012; Xie and Tackley, 2004; Xu et al., 2008). In situ equations of state studies indicate that basalt is denser than average mantle and would tend to pile up at the core–mantle boundary (Hirose et al., 2005). Basalt-rich piles may be swept up by mantle convection, and may explain lower mantle anomalies with boundaries that are sharp, that is, of apparently non-thermal origin (Ni et al., 2002; Sun et al., 2007), and primitive signatures in mantle geochemistry (Kellogg et al., 1999).

2.17.3.4 Phase

The mantle is made of several different phases with distinct elastic properties. As temperature varies, the relative proportions and compositions of these phases change, producing an additional contribution to the laterally varying structure (Figure 13). This effect has been discussed in terms of thermally induced phase transformations (Anderson, 1987). The magnitude of the effect is

$$\left(\frac{\partial V}{\partial T} \right)_{P, \text{phase}} \approx f \left(\frac{\partial P}{\partial T} \right)_{eq} \frac{\Delta V}{\Delta P} \quad [12]$$

where f is the volume fraction of the mantle composed of the transforming phases, ΔV is the velocity contrast between them, ΔP is the pressure range over which the transition occurs, and the derivative on the right-hand side is the effective Clapeyron

slope (Stixrude and Lithgow-Bertelloni, 2007). The effect is largest for sharp transitions, such as the olivine to wadsleyite transition, and in this case may also be described in terms of the topography of the transition. It is sensible to describe lateral variations in velocity caused by phase equilibria in terms of topography when the topography exceeds the width of the phase transformation

$$\left(\frac{\partial P}{\partial T} \right)_{eq} \Delta T > \Delta P \quad [13]$$

where ΔT is the anticipated magnitude of lateral temperature variations. But the influence of phase transformations is also important for broad transitions such as pyroxene to garnet. In the upper mantle, most phase transitions have positive Clapeyron slopes. This means that, except in the vicinity of the 660-km discontinuity, phase transitions systematically increase the temperature dependence of seismic wave velocities throughout the upper 800 km of the mantle.

Lateral variations in phase have been invoked to explain some of the unusual features of the deep lower mantle, including the anti-correlation in bulk and shear-wave velocities and large values of R mentioned earlier (Davies et al., 2012; Iitaka et al., 2004; Oganov and Ono, 2004; Tsuchiya et al., 2004b; Wentzcovitch et al., 2006). As perovskite transforms to post-perovskite, the shear modulus increases while the bulk modulus decreases. Lateral variations in the relative abundance of these two phases, caused, for example, by lateral variations in temperature, produce anti-correlated variations in V_s and V_p . Because the stability of the post-perovskite phase is restricted to the D'' layer, it is not clear whether this mechanism can explain all the anomalous features of lower mantle tomography, which appear to extend over a much greater depth interval.

The high spin to low spin transition in iron has a significant effect on the physical properties of ferropericlase, perovskite,

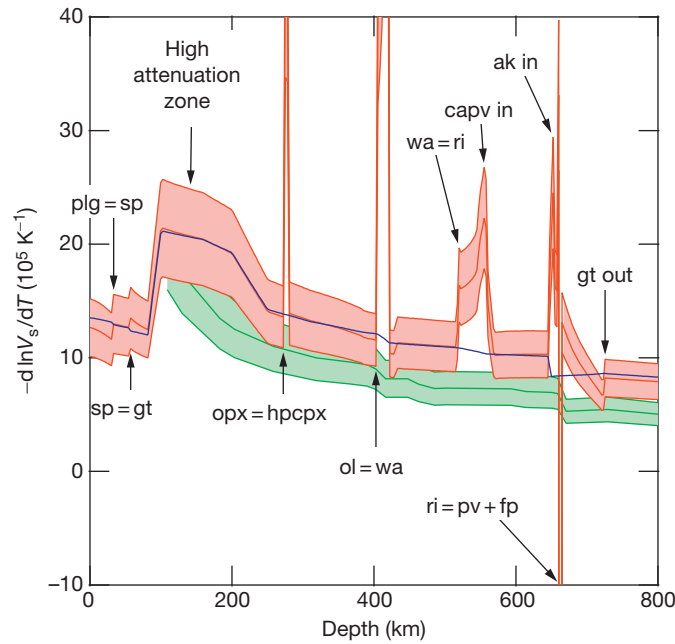


Figure 13 The variation of shear-wave velocity with temperature in pyrolite (red) including the effects of pressure, temperature, phase transformations, and anelasticity according to the model QR19 (Romanowicz, 1995) and $\alpha = 0.25$, and variation of Q with temperature given by $H^* = 430 \text{ kJ mol}^{-1}$. The blue curve shows the derivative neglecting the influence of phase transformations. The green curve shows a similar calculation (Cammarano et al., 2003) except that the effect of phase transformations is neglected. Reproduced from Stixrude L and Lithgow-Bertelloni C (2007) Influence of phase transformations on lateral heterogeneity and dynamics in Earth's mantle. *Earth and Planetary Science Letters* 263: 45–55.

and post-perovskite (Badro et al., 2003, 2004; Cohen et al., 1997; Li et al., 2005; Pasternak et al., 1997; Stackhouse et al., 2006, 2007). Theoretical and experimental results show that the transition is spread out over hundreds of kilometers in depth at mantle temperatures and should affect laterally varying structure over much of the lower mantle (Tsuchiya et al., 2006). Within the transition interval, the bulk modulus and, therefore, the P-wave velocity are reduced (Crowhurst et al., 2008), while the thermal expansivity is enhanced (Wu et al., 2009), an aspect of lower mantle physics that has been included in dynamical models of plume upwelling (Bower et al., 2009).

2.17.4 Anisotropy

2.17.4.1 Overview

Anisotropy is a potentially powerful probe of mantle dynamics because it is produced by deformation. In dislocation creep, the easiest crystallographic slip plane tends to align with the plane of flow, and the easiest slip direction with the direction of flow. As all mantle minerals are elastically anisotropic (Figure 14), this preferred orientation or texturing produces bulk anisotropy that is measurable by seismic waves. This mechanism for producing anisotropy is often referred to as lattice-preferred orientation. Another mechanism is shape-preferred orientation in which the rheological contrast between the materials making up a composite causes them to be arranged inhomogeneously on deformation. Heterogeneous arrangements familiar from structural geology, including foliation and lineation, lead to anisotropy for seismic

waves with wavelengths much longer than the scale length of heterogeneity.

Anisotropy is pervasive in the continental crust, and significant in the upper mantle, the D'' layer, and the inner core, the latter of which has been discussed earlier in the section on the core. Anisotropy may also exist in the transition zone as indicated by global (Montagner and Kennett, 1996; Trampert and van Heijst, 2002) and regional (Fouch and Fischer, 1996) seismic models.

2.17.4.2 Upper Mantle

Anisotropy is well developed in the uppermost mantle. Studies of the seismic structure of this region, the texture of mantle samples, and the elastic properties of the constituent minerals have led to a simple first-order picture. Convective flow in the upper mantle preferentially aligns olivine crystals such that the seismically fast direction is parallel to the flow direction (Christensen and Salisbury, 1979; Mainprice et al., 2000). Two seismological signals are often distinguished, associated with different datasets and modeling strategies. Horizontally propagating shear waves travel at two different velocities depending on the direction of polarization: the faster one is horizontal with V_{SH} and the slower one is vertical with V_{SV} . The difference in the velocity of the two polarizations is also referred to as shear-wave splitting. The shear-wave velocity also depends on the direction of propagation, and this is usually referred to as azimuthal anisotropy. Azimuthal anisotropy is also detected along vertically propagating paths via shear-wave splitting (Silver, 1996).

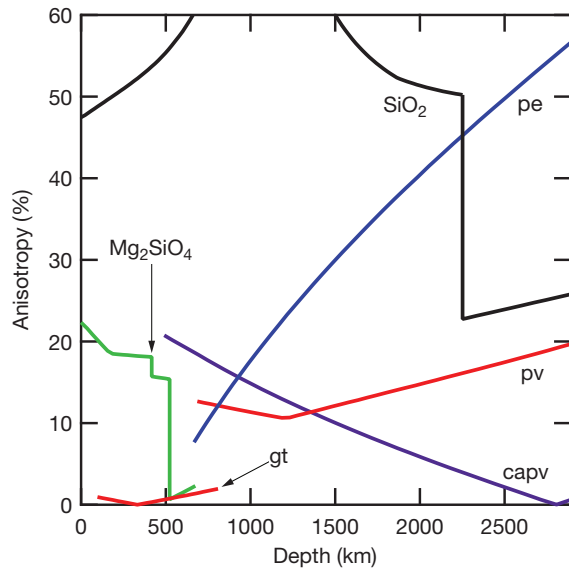


Figure 14 Single crystal azimuthal anisotropy of S-wave velocity in mantle minerals plotted, except for silica, over their pressure range of stability in pyrolite. The discontinuous changes in silica and Mg_2SiO_4 are due to phase transformations. The breaks in slope in garnet (pyroxene), perovskite, and calcium perovskite are due to interchanges in the fastest and slowest directions where the anisotropy passes through zero (Karki et al., 1997a). Reproduced from Mainprice D, Barruol G, and Ben Ismail W (2000) The seismic anisotropy of the Earth's mantle: From single crystal to polycrystal. In: Karato S, et al. (eds.) *Earth's Deep Interior: Mineral Physics and Tomography from the Atomic to the Global Scale*. Washington, DC: American Geophysical Union.

In detail, the picture of upper mantle anisotropy is much richer than this first-order pattern. There are unexplained anomalies even in regions where the pattern of flow is presumably simple and large scale such as the Pacific basin. For example, the fast direction does not align everywhere with the direction of present-day plate motions (Montagner and Guillot, 2002; Tanimoto and Anderson, 1984). The magnitude of $V_{\text{SH}} - V_{\text{SV}}$ varies spatially in a way that does not correlate simply with lithosphere age: the difference is maximum near the center of the north Pacific (Ekstrom and Dziewonski, 1998). At subduction zones, the fast direction is sometimes parallel rather than normal to the trench (Fouch and Fischer, 1996; Long and Silver, 2008; Russo and Silver, 1994). Explanations of these features will come from a better understanding of the development of texture in large-scale mantle flow (Chastel et al., 1993; Ribe, 1989); the preferred slip planes and critical resolved shear stresses in olivine and how these depend on stress, temperature, pressure, and impurities (Jung and Karato, 2001; Mainprice et al., 2005); how stress and strain are partitioned between lithosphere and asthenosphere; and the relative importance of dislocation versus diffusion creep (Karato, 1992; van Hunen et al., 2005). Some alternative explanations for trench-parallel fast directions feature the role of low-abundance, but high-intrinsic-anisotropy serpentine at the top of the subducting slab (Katayama et al., 2009; Mookherjee and Capitani, 2011), and the tilting, on subduction, of the dominant olivine fabric beneath the slab (Song and Kawakatsu, 2012).

2.17.4.3 D'' Layer

The D'' layer is also substantially anisotropic (Lay et al., 1998b; Panning and Romanowicz, 2004). The minerals that make up this region have large single crystal anisotropies, with ferropericlase having the largest (Karki et al., 2001; Stackhouse et al., 2005; Wentzcovitch et al., 2006; Figure 14). The anisotropy of periclase depends strongly on pressure and actually reverses sense near 20 GPa: the directions of the fastest and slowest elastic wave propagation inter-change (Karki et al., 1997a; Marquardt et al., 2009). This behavior emphasizes the importance of experimental measurements and first-principles predictions of elasticity at the relevant pressures. The easy glide planes of the minerals in D'' are still uncertain. If one assumes that the easy glide planes are the same as those seen in ambient pressure experiments or analog materials, anisotropy produced by lattice-preferred orientation in neither ferropericlase nor perovskite can explain the dominant pattern $V_{\text{SH}} > V_{\text{SV}}$ seen in seismology (Karato, 1998; Stixrude, 1998). In the case of post-perovskite, theory and two different experiments have come to orthogonal conclusions (Carrez et al., 2007; Merkel et al., 2007; Miyagi et al., 2010). A recent study combining assumed deformation mechanisms, model mantle flow fields, and ray tracing concluded that seismic observations of anisotropy in D'' could be explained by post-perovskite if the dominant slip plane is (0 1 0) (Nowacki et al., 2013). One must be cautious, because the sense and magnitude of anisotropy depends strongly on the assumed easy glide plane and also on still uncertain details of the single-crystal elasticity.

2.17.5 Attenuation and Dispersion

2.17.5.1 Overview

Earth is not a perfectly elastic medium, even at seismic frequencies. There are two important consequences. Attenuation refers to the loss of amplitude of the elastic wave with propagation. Dispersion refers to the dependence of the elastic-wave velocity on the frequency. It can be shown that attenuation and dispersion are intimately related. Indeed, the importance of attenuation in Earth first alerted seismologists to the dispersion that should yield a difference in velocities between low-frequency normal mode oscillations and higher frequency body waves. The magnitude of attenuation is measured by the inverse quality factor Q^{-1} , the fractional energy loss per cycle.

From the mineralogical point of view, attenuation is potentially important as a very sensitive probe of temperature and minor element composition (Karato, 1993; Karato and Jung, 1998). Because attenuation is caused at the atomic scale by thermally activated processes, its magnitude is expected to depend exponentially on temperature. By analogy to the viscosity, the attenuation is also expected to depend strongly on the concentration of water, although there are as yet no experimental constraints on this effect. But with this promise come formidable challenges. Dissipative processes depend on defect concentrations and dynamics and/or the presence of multiple scales, such as grains and grain boundaries. These are much more challenging to study in the laboratory than equilibrium thermodynamic properties such as the elastic response. As an example of the connection between attenuation and

non-equilibrium properties, a recent study has demonstrated bulk attenuation associated with the kinetics of phase transformations (Li and Weidner, 2008).

2.17.5.2 Influence of Temperature

The most thorough study of attenuation is of olivine aggregates, specially fabricated to have an approximately uniform grain size and minimal dislocation density (Gribb and Cooper, 1998; Jackson et al., 2002). Whether such samples are representative of the mantle is an important question, although at this stage, when experimental data are so few, the need for precise and reproducible results is paramount. Measurements on analog materials will also continue to be important (McCarthy et al., 2011). The key results of Jackson et al. (2002) within the seismic frequency band (~ 1 –100 s) and in the limit of small attenuation, are consistent with the following relations

$$Q^{-1}(P, T, \omega) = Ad^{-m}\omega^{-\alpha} \exp\left(-\alpha \frac{E^* + PV^*}{RT}\right) \quad [14]$$

$$V_S(P, T, \omega) = V_S(P, T, \infty) \left[1 - \frac{1}{2} \cot\left(\frac{\alpha\pi}{2}\right) Q^{-1}(P, T, \omega)\right] \quad [15]$$

where ω is the frequency, d is the grain size, $m=0.28$ is the grain size exponent, $\alpha=0.26$, $E^*=430 \text{ kJ mol}^{-1}$ is the activation energy, V^* is the activation volume, and R is the gas constant. For the experimental value of α , the factor multiplying Q^{-1} in eqn [15] has the value 1.16. The activation volume is currently unconstrained, which means the influence of pressure on attenuation is highly uncertain, although this quantity has been measured for other rheological properties such as viscosity and climb-controlled dislocation creep in olivine. Partial melt in the amount of 1% increases Q^{-1} by a factor that depends weakly on frequency and grain size and is approximately 2 in the seismic band and for plausible grain sizes (1–10 mm) (Faul et al., 2004). The influence of crystallographically bound hydrogen on the attenuation is currently unconstrained, although it is known that the viscosity decreases with increasing hydrogen concentration (Mei and Kohlstedt, 2000a,b). The second relation makes explicit the relationship between attenuation and dispersion. Equations [14] and [15] are consistent with earlier theories developed primarily on the basis of seismological observations and the idea of a distribution of dissipative relaxation times in solids (Anderson, 1989).

An important consequence of eqn [15] is that, if the value of the frequency exponent is known, the magnitude of the dispersion depends only on the value of Q^{-1} . This means that it is possible to directly relate seismological velocity models to experimental measurements in the elastic limit. Knowing the seismological value of Q^{-1} and V , one may compute $V(\infty)$ and compare this directly with high-frequency experiments or first-principles calculations. Alternatively, one may correct elastic wave velocities according to the seismological value of Q^{-1} in order to compare them with the seismological velocity model (Stixrude and Lithgow-Bertelloni, 2005b). These considerations are most important in the low-velocity zone where $1000/Q$ reaches 20 and the difference in velocity between the elastic limit and the seismic band may be as great as 2%.

Attenuation enhances the temperature dependence of seismic-wave velocities and is important to consider in the interpretation of seismic tomography (Karato, 1993). The temperature derivative of eqn [15] is

$$\frac{\partial \ln V(\omega)}{\partial T} = \frac{\partial \ln V(\infty)}{\partial T} - \frac{1}{2} \cot\left(\frac{\alpha\pi}{2}\right) Q^{-1} \frac{H^*}{RT^2} \quad [16]$$

where $H^*=E^*+PV^*$ is the activation enthalpy. For $\alpha=0.26$, $H^*=430 \text{ kJ mol}^{-1}$, $1000/Q=10$, and $T=1600 \text{ K}$, the second term is $-6 \times 10^{-5} \text{ K}^{-1}$, nearly as large as the elastic temperature derivative neglecting the influence of phase transformations (Figure 11).

Laboratory studies predict large lateral variations in attenuation in the mantle. Over a range of temperature 1500–1600 K, the attenuation varies by a factor of 2. This extreme sensitivity promises powerful constraints on the temperature structure of the mantle that are complementary to those derived from the elastic wavespeeds. Attenuation tomography reveals a decrease of approximately one order of magnitude in Q^{-1} with increasing lithospheric age from 0 to 100 Ma in the Pacific low-velocity zone (Romanowicz, 1998). Arcs appear to have exceptionally high attenuation (Barazangi and Isacks, 1971; Roth et al., 2000), and subduction zones have low attenuation (Dalton et al., 2008). Unraveling the relative contributions of partial melt, water concentration, and other factors (grain size?) to this observation will provide unique constraints on the process of arc magma generation. This program is still limited by the lack of experimental data on the influence of water content on Q .

2.17.5.3 Speculations on the Influence of Pressure

Comparisons of laboratory determinations to radial seismological models of Q^{-1} reveal some surprises. The comparison is hampered by the fact that there are currently no experimental data at elevated pressure. Two models have been explored in the literature: eqn [14] with the activation volume assumed to be independent of pressure and temperature, and the homologous temperature formulation in which activated properties are assumed to scale with the ratio of the absolute temperature to melting temperature (Weertman, 1970)

$$Q^{-1}(P, T, \omega) = Ad^{-m}\omega^{-\alpha} \exp\left[-\alpha \frac{gT_m(P)}{T}\right] \quad [17]$$

where $T_m(P)$ is the melting temperature as a function of pressure, and the parameter g is assumed to be constant. Neither of these models resembles the variation of Q^{-1} in the vicinity of the low-velocity zone (Figure 15). The high-attenuation zone in the mantle is much more sharply defined at its lower boundary than either eqn [14] or [17]. While the limited vertical resolution of the seismological Q models cannot be overlooked, the comparison seems to imply that either (1) eqns [14] and [17] do not represent the pressure dependence of activated processes, at least not those responsible for dissipation in the seismic band in the mantle, (2) there is a change in the composition or phase of the mantle at this depth, for example, a change in water content or partial melt fraction, or (3) there is a change in the physical mechanism of attenuation at the base of the low-velocity zone. Faul and Jackson (2005)

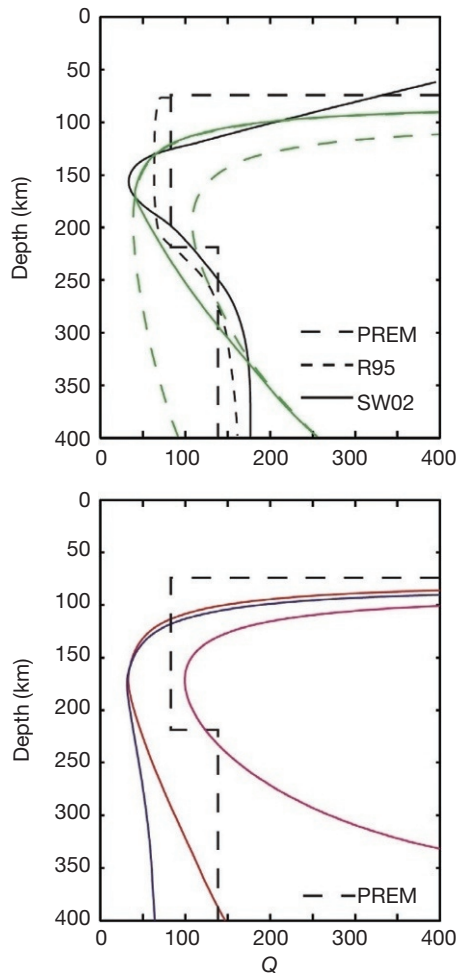


Figure 15 Quality profiles calculated assuming a range of temperatures and activation volumes and grain size either independent of depth (dashed curves in upper figure, rightmost pink curve in lower figure), or increasing by a factor of 5 (solid curve in upper figure) or 2 (red and blue curves in lower figure) as a function of depth, compared with seismological attenuation models (Dziewonski and Anderson, 1981; Romanowicz, 1995; Selby and Woodhouse, 2002). Reproduced from Faul UH and Jackson I (2005) The seismological signature of temperature and grain size variations in the upper mantle. *Earth and Planetary Science Letters* 234: 119–134.

have proposed that the base of the low-velocity zone represents a rapid change in grain size with increasing depth, although the mechanism by which such a change could occur is uncertain.

2.17.6 Conclusions

Over the last decade, studies of the seismic properties of major Earth-forming materials have dramatically expanded in scope. The field has moved from measurements of the elastic properties of individual minerals at elevated pressure and temperature to now include studies of deformation mechanisms and their relationship to the development of anisotropy, attenuation and dispersion, and the interplay between phase

equilibria and elasticity in mantle assemblages approaching realistic bulk compositions. Major challenges remain in each of the mantle's regions. The upper mantle structure is remarkably rich and surprisingly full of features that resist explanation, such as the discontinuity structure and the high-velocity gradient. Phase transformations are ubiquitous in the transition zone; there is no depth at which a transformation is not in progress, so that understanding this region will require the continued development of thermodynamic models of the mantle that are simultaneously able to capture phase equilibria and physical properties. The lower mantle still lies beyond the reach of many experimental techniques for measuring the elastic constants, and most of our knowledge of elasticity in this region comes from first-principles theory. New physics in the lower mantle, including high-spin to low-spin transitions, the post-perovskite transition, and valence state changes promise new solutions to problems such as the anti-correlation between bulk and shear-wave velocity variations, and fertile ground for new ideas. Many classic problems of the core, including its composition and temperature, seem to be yielding to new approaches and promise new constraints on the origin and evolution of Earth's deepest layer. At the same time, the seismic structure of the inner core, including its anisotropy, heterogeneity, and layering, remains enigmatic.

Acknowledgments

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2.18 Constitutive Equations, Rheological Behavior, and Viscosity of Rocks

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2.18.1 Introduction

The rheological behavior of mantle rocks determines the mechanical response of lithospheric plates and the nature of convective flow in the deeper mantle. Geodynamic models of these large-scale processes require constitutive equations that describe rheological properties of the appropriate mantle rocks. The forms of such constitutive equations (flow laws or combinations of flow laws) are motivated by micromechanical analyses of plastic deformation phenomena based on physical processes such as ionic diffusion, dislocation migration, and grain-boundary sliding. Critical parameters in flow laws appropriate for rock deformation such as the dependence of strain rate on stress, grain size, temperature (activation energy), and pressure (activation volume) must be determined from well-designed, carefully executed laboratory experiments. Geophysical observations of the mechanical behavior of Earth's mantle in response to changes in the stress environment due, for example, to an earthquake or the retreat of a glacier provide tests of the applicability of the resulting constitutive equations to deformation occurring under geologic conditions.

Confident extrapolation of flow laws determined under laboratory conditions requires an understanding of the physical processes involved in deformation. Minerals and rocks deform plastically by a number of different mechanisms, each of which requires defects in the crystalline structure. Diffusion creep involves the movement of atoms or ions and thus of point defects; dislocation creep entails the glide and climb of line defects; grain-boundary sliding necessitates motion along planar defects. Within any deformation regime, more than one deformation process may be important. For example, diffusion creep can be divided into one regime dominated by diffusion along grain boundaries and another dominated by diffusion through grain interiors (the so-called grain matrix). Grain size, temperature, and pressure dictate which of these two processes is more important. Likewise, in dislocation creep, deformation can be divided into low-temperature and high-temperature regimes, with glide of dislocations controlling the rate of deformation in the former and climb of dislocations in the latter. As temperature decreases, differential stress necessarily increases if deformation is to continue at a given rate.

Plastic deformation is a thermally activated, kinetic, and irreversible process. Experimentalists frame laboratory investigations

of plastic deformation in terms of strain rate as a function of differential stress, temperature, pressure, and grain size and other microstructural and chemical parameters. In contrast, geodynamicists cast plasticity in terms of viscosity, the ratio of stress to strain rate. In both cases, flow laws or constitutive equations describe the relationships between these parameters, thus providing the basis for extrapolating from laboratory to Earth conditions. Tests of the appropriateness of laboratory-derived flow laws to processes occurring in Earth at much slower strain rates (higher viscosities) – and thus necessarily much lower stresses and/or much lower temperatures and/or much coarser grain sizes – include comparisons of microstructures observed in experimentally deformed samples with those in naturally deformed rocks and of viscosities derived from laboratory experiments with those determined from geophysical observations.

This chapter, therefore, starts with an examination of the role of defects in plastic deformation, including a discussion of the influence of water-derived point defects on kinetic processes. Next, a section on some of the important mechanisms of deformation introduces constitutive equations that describe plastic flow by linking thermomechanical parameters such as strain rate, differential stress, temperature, pressure, and water fugacity with structural parameters such as dislocation density, grain size, and melt fraction. Finally, profiles of viscosity versus depth in the upper mantle are used to test the applicability of flow laws determined from micromechanical models and laboratory experiments to plastic flow taking place deep beneath Earth's surface.

2.18.2 Role of Lattice Defects in Deformation

Defects in rocks are essential for plastic deformation to proceed. Zero-dimensional or point defects (specifically vacancies and self-interstitials) allow flow by diffusive transport of ions, one-dimensional or line defects (dislocations) permit deformation by glide and climb, and two-dimensional or planar defects (grain–grain interfaces) facilitate deformation involving grain-boundary sliding and migration. More than one type of defect may be simultaneously involved in deformation. For example, diffusion creep involves not only diffusion by a point defect mechanism but also sliding on grain boundaries (Raj and Ashby, 1971), dislocation processes also frequently couple with grain-boundary sliding (Langdon, 1994), and dislocation creep necessitates glide on several slip systems often combined with climb (Groves and Kelly, 1969; Paterson, 1969; von Mises, 1928). In addition, dynamic recrystallization frequently acts as a recovery mechanism, producing a new generation of dislocation-free grains that are more easily deformed than the parent grains (e.g., de Bresser et al., 2001; Drury, 2005; Platt and Behr, 2011; Tullis and Yund, 1985). In this section, some fundamental aspects of point defects, dislocations, and grain boundaries are introduced as background for discussing the rheological behavior of rocks and the associated constitutive equations.

2.18.2.1 Point Defects: Thermodynamics and Kinetics

2.18.2.1.1 Thermodynamics

At temperatures above absolute zero, crystalline grains in thermodynamic equilibrium contain finite populations of vacancies and self-interstitials. Although the enthalpy of a crystal

increases linearly with the addition of vacancies or self-interstitials, the entropy decreases nonlinearly. Hence, the Gibbs free energy of a crystal is minimized not when the crystal is perfect (i.e., defect-free) but rather when the crystal contains a finite concentration of vacancies and self-interstitials (i.e., when the crystal is imperfect) (see, e.g., Devereux, 1983, pp. 296–300). In metals, the concentrations of these point defects in thermodynamic equilibrium are determined by temperature and pressure through their Gibbs free energies of formation (Schmalzried, 1981, pp. 37–38). In ionic materials, the situation is more complicated because the concentrations of the different types of point defects are coupled through the necessity for electroneutrality, which requires that the sum of the concentrations of the various types of positively charged point defects equals the sum of the concentrations of all of the negatively charged point defects (Schmalzried, 1981, pp. 38–42). The concentration of one type of positively charged point defect often greatly exceeds the concentrations of the other positively charged point defects; a similar situation frequently exists for negatively charged defects. This combination of positive and negative defects defines the majority point defects or the defect type. The charge neutrality condition is then approximated by equating the concentration of the positively charged to the concentration of the negatively charged majority point defects. An example serves to illustrate the salient elements of point defect thermodynamics.

Consider the case of a simple metal oxide, MeO, where Me is an ion such as Mg, Ni, Co, Mn, or Fe. Structural elements for this system include $\text{Me}_{\text{Me}}^{\times}$, $\text{O}_{\text{O}}^{\times}$, $\text{Me}_{\text{Me}}^{\bullet}$, $\text{Me}_i^{\bullet}$, $\text{V}_{\text{O}}^{\bullet}$, $\text{V}_{\text{Me}}^{\bullet}$, and $\text{O}_i^{\bullet}$. The first two entries are termed ‘regular structural elements’ and the last five are called ‘irregular structural elements’ or point defects in the ideal crystal lattice. The Kröger–Vink (1956) notation is used to indicate the atomic species, A, occupying a specific crystallographic site, S, and having an effective charge, C, relative to the ideal crystal lattice: A_S^C . In this nomenclature, the superscripted symbols $\times$, $\bullet$, and $/$ indicate neutral, one positive, and one negative effective charges. Vacant sites are denoted by a V, and ions located at interstitial sites are indicated by a subscripted i. The defect $\text{Me}_{\text{Me}}^{\bullet}$ corresponds to a 3+ ion sitting at a site normally occupied by a 2+ ion, such as a ferric iron in a ferrous iron site. In a strict sense, charge neutrality is given by

$$[\text{Me}_{\text{Me}}^{\bullet}] + 2[\text{V}_{\text{O}}^{\bullet}] + 2[\text{Me}_i^{\bullet}] = 2[\text{V}_{\text{Me}}^{\bullet}] + 2[\text{O}_i^{\bullet}] \quad [1a]$$

where the square brackets, [], indicate molar concentration. In a Mg-rich system, one possible disorder type is the combination $\text{Me}_i^{\bullet}$ and $\text{V}_{\text{Me}}^{\bullet}$ (Catlow et al., 1994), such that the charge neutrality condition is approximated as

$$[\text{Me}_i^{\bullet}] = [\text{V}_{\text{Me}}^{\bullet}] \quad [1b]$$

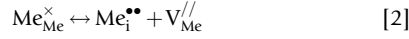
In contrast, in an Fe-rich quasi-binary material such as (Mg,Fe)O, likely majority point defects are $\text{Fe}_{\text{Me}}^{\bullet}$ and $\text{V}_{\text{Me}}^{\bullet}$ (Hilbrandt and Martin, 1998), yielding the charge neutrality condition

$$[\text{Fe}_{\text{Me}}^{\bullet}] = 2[\text{V}_{\text{Me}}^{\bullet}] \quad [1c]$$

where $\text{Fe}_{\text{Me}}^{\bullet}$ is often written as $\text{h}^{\bullet}$, indicating a highly mobile electron hole localized at a Fe^{2+} site.

To obtain expressions that give the dependences of point defect concentrations on thermodynamic variables such as

temperature, pressure, and component activities, reaction equations are needed. The first reaction equation should involve the majority point defects. In the case of the Frenkel disorder type given by eqn [1b], the appropriate reaction starts with a regular structural element resulting in



for which the law of mass action yields

$$a_{\text{Me}_{\text{Me}}^{\times}} a_{\text{V}_{\text{Me}}^{\prime\prime}} = a_{\text{Me}_{\text{i}}^{\bullet\bullet}} K_2 \quad [3a]$$

where $K_2 = K_F$ is the reaction constant for the reaction in eqn [2]. Since the activity of $\text{Me}_{\text{Me}}^{\times}$ is little affected by the presence of a small concentration of point defects (typically $< 10^{-3}$), $a_{\text{Me}_{\text{Me}}^{\times}} \approx [\text{Me}_{\text{Me}}^{\times}] \approx 1$. Likewise, for ideally dilute solutions of point defects, the activities of the point defects can be replaced by their concentrations such that eqn [3a] becomes

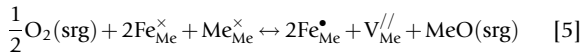
$$[\text{Me}_{\text{i}}^{\bullet\bullet}] [\text{V}_{\text{Me}}^{\prime\prime}] = K_F = \exp \frac{-G_F}{RT} \quad [3b]$$

where G_F is the Gibbs free energy for the reaction in eqn [2] and RT has the usual meaning. This reaction describes the formation of the so-called Frenkel point defects (a vacancy–interstitial pair). If the charge neutrality condition in eqn [1b] and the mass action equation in eqn [3b] are combined, the dependence on temperature and pressure of the concentrations of the Frenkel defects is

$$[\text{Me}_{\text{i}}^{\bullet\bullet}] = [\text{V}_{\text{Me}}^{\prime\prime}] = \sqrt{K_F} = \exp \frac{-G_F}{2RT} \quad [4]$$

Frenkel majority point defects are an example of a thermal disorder type, that is, the concentrations of these point defects depend on temperature and pressure but not on the activities of the components. A second example of thermal disorder occurs if Schottky point defects, $\text{V}_{\text{Me}}^{\prime\prime}$ and $\text{V}_{\text{O}}^{\bullet\bullet}$, are the majority point defects.

For the disorder type given by eqn [1c], the appropriate reaction involves a regular structural element plus a neutral crystal component to yield



where the oxygen is provided from a site of repeatable growth (srg) such as a dislocation, grain boundary, or crystal–gas interface (surface). The law of mass action yields

$$[\text{Fe}_{\text{Me}}^{\bullet\bullet}]^2 [\text{V}_{\text{Me}}^{\prime\prime}] a_{\text{MeO}} = [\text{Fe}_{\text{Me}}^{\times}]^2 [\text{Me}_{\text{Me}}^{\times}] f_{\text{O}_2}^{1/2} K_5 \quad [6]$$

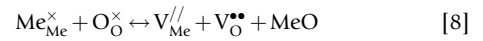
where f_{O_2} is the oxygen fugacity. If the charge neutrality condition in eqn [1c] is now substituted into eqn [6] and the approximation $[\text{Me}_{\text{Me}}^{\times}] \approx a_{\text{MeO}} = 1$ is made, then

$$\begin{aligned} [\text{Fe}_{\text{Me}}^{\bullet\bullet}] &= 2 [\text{V}_{\text{Me}}^{\prime\prime}] = \sqrt[3]{2} [\text{Fe}_{\text{Me}}^{\times}]^{2/3} f_{\text{O}_2}^{1/6} K_5^{1/3} \\ &= \sqrt[3]{2} [\text{Fe}_{\text{Me}}^{\times}]^{2/3} f_{\text{O}_2}^{1/6} \exp \frac{-G_5}{3RT} \end{aligned} \quad [7]$$

Thus, if a neutral crystal component is added from a site of repeatable growth, the concentrations of the majority point defects will depend not only on pressure and temperature but also on component activities, often referred to as an activity-dependent disorder type. In this case, it should be noted that

the material will be nonstoichiometric with typically $[\text{V}_{\text{Me}}^{\prime\prime}] \gg [\text{V}_{\text{O}}^{\bullet\bullet}]$. Also, a comparison of eqn [4] with eqn [7] demonstrates that the functional form and the magnitude of the concentration of $\text{V}_{\text{Me}}^{\prime\prime}$ depend on the charge neutrality condition.

Since $[\text{V}_{\text{O}}^{\bullet\bullet}]$ is generally several orders of magnitude smaller than $[\text{V}_{\text{Me}}^{\prime\prime}]$, O diffuses much more slowly than Me, at least through the interiors of grains. Consequently, as discussed later in the text, the rate of diffusion creep (specifically, Nabarro–Herring creep) and rate of dislocation climb are limited by the rate of O diffusion. Hence, it is important to examine the dependence of the concentration of $\text{V}_{\text{O}}^{\bullet\bullet}$ on temperature, pressure, and oxygen fugacity. Since the dependence of the concentration of $\text{V}_{\text{Me}}^{\prime\prime}$ on these parameters has been determined earlier in the text, the formulation of a reaction involving $\text{V}_{\text{O}}^{\bullet\bullet}$ and $\text{V}_{\text{Me}}^{\prime\prime}$ provides a good starting point. The point defects $\text{V}_{\text{O}}^{\bullet\bullet}$ and $\text{V}_{\text{Me}}^{\prime\prime}$ are related via the Schottky formation reaction



It should be emphasized that it is essential in reaction equations such as eqn [8] that the number and identity of the atomic species, the crystallographic sites, and the effective charges (recall A_{S}^{C}) be the same on the two sides of the reaction equation. The law of mass action for eqn [8] reads

$$[\text{V}_{\text{Me}}^{\prime\prime}] [\text{V}_{\text{O}}^{\bullet\bullet}] = K_S = \exp \frac{-G_S}{RT} \quad [9]$$

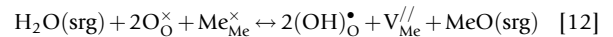
again using the approximations $a_{\text{Me}_{\text{Me}}^{\times}} \approx a_{\text{O}_{\text{O}}^{\times}} \approx 1$ with a_{MeO} equal to unity since MeO is present. For the Frenkel thermal disorder type given by eqn [1b], $[\text{Me}_{\text{i}}^{\bullet\bullet}] = [\text{V}_{\text{Me}}^{\prime\prime}]$, if eqn [9] is now combined with eqn [4], then

$$[\text{V}_{\text{O}}^{\bullet\bullet}] = [\text{V}_{\text{Me}}^{\prime\prime}]^{-1} K_S = \frac{K_S}{\sqrt{K_F}} = \exp \frac{-(G_S - G_F/2)}{RT} \quad [10]$$

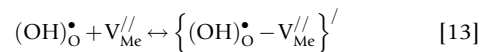
For the activity-dependent disorder type given by eqn [1c], $[\text{Fe}_{\text{Me}}^{\bullet\bullet}] = 2[\text{V}_{\text{Me}}^{\prime\prime}]$, if eqn [9] is combined with eqn [7], then

$$\begin{aligned} [\text{V}_{\text{O}}^{\bullet\bullet}] &= [\text{V}_{\text{Me}}^{\prime\prime}]^{-1} K_S = \sqrt[3]{4} [\text{Fe}_{\text{Me}}^{\times}]^{-2/3} f_{\text{O}_2}^{-1/6} \frac{K_S}{K_5^{1/3}} \\ &= \sqrt[3]{4} [\text{Fe}_{\text{Me}}^{\times}]^{-2/3} f_{\text{O}_2}^{-1/6} \exp \frac{-(G_S - G_5/3)}{RT} \end{aligned} \quad [11]$$

Under hydrous conditions, additional point defects must be considered. Hydrogen ions, that is, protons, $\text{p}^{\bullet}$, occupy interstitial sites, $\text{H}_{\text{i}}^{\bullet}$, near oxygen ions, thus corresponding to hydroxyl point defects, $(\text{OH})_{\text{O}}^{\bullet}$. This water-derived point defect can be introduced through dissociation of a water molecule by the reaction



In addition, point defect associates such as those produced between $(\text{OH})_{\text{O}}^{\bullet}$ and $\text{V}_{\text{Me}}^{\prime\prime}$ can form



where the curly brackets, $\{ \}$, indicate a defect associate. This and other defect associates and $(\text{OH})_{\text{O}}^{\bullet}$ must now be included in the charge neutrality equation, eqn [1a]. Note that the defect associate $\{(\text{OH})_{\text{O}}^{\bullet} - \text{V}_{\text{Me}}^{\prime\prime}\}^{\prime}$ is sometimes written in shorthand

as H_{Me}^+ . It should be kept in mind that, as stated in the preceding text, protons occupy interstitial sites that are located very near oxygen ions giving rise to hydroxyl point defects; protons (or equivalently hydroxyl defects) can form defect associates with metal vacancies; however, they do not literally occupy metal vacancies. New disorder types such as

$$[(OH)_O^\bullet] = \left[\left\{ (OH)_O^\bullet - V_{Me}^{//} \right\}^{\prime} \right] \quad [14]$$

and

$$[Fe_{Me}^\bullet] = \left[\left\{ (OH)_O^\bullet - V_{Me}^{//} \right\}^{\prime} \right] \quad [15]$$

must also be considered. A summary of the dependencies of the concentrations of various point defects on oxygen fugacity and water fugacity for the system MeO is provided in Table 1 for a range of charge neutrality conditions.

2.18.2.1.2 Kinetics

Diffusion of atoms and ions through crystalline solids takes place by the movement of point defects, namely, vacancies and self-interstitials. That is, ionic diffusion takes place by a vacancy or interstitial mechanism. Here, the discussion focuses on vacancies; a parallel analysis applies for self-interstitials. Since the fraction of vacant sites, X_V , on any specific sublattice is small, typically $<10^{-3}$ to $\ll 10^{-3}$, vacancies diffuse orders of magnitude more rapidly than the ions on that sublattice. From the point of view of a vacancy, all of the neighboring sites are available, while from the perspective of an ion, possibly one but more likely no neighboring sites are available at any particular moment. This connection between the movement of ions and that of vacancies leads to the following relationship between the diffusion coefficient for ions, D_{ion} , and that for vacancies, D_V :

$$X_{ion}D_{ion} = X_VD_V \quad [16a]$$

where X_{ion} is the fraction of sites on a given sublattice occupied by the ions associated with that sublattice. Since $X_{ion} = (1 - X_V) \approx 1$, eqn [16a] is usually approximated as

$$D_{ion} \approx X_VD_V \quad [16b]$$

consequently,

$$D_{ion} \ll D_V \quad [16c]$$

that is, vacancies diffuse orders of magnitude faster than ions because $X_V \ll 1$.

One consequence of the rapid diffusion of vacancies (as well as of electron holes) is that equilibrium concentrations of vacancies are attained relatively rapidly in response to changes

in oxygen partial pressure or oxide activity, typically in much less than an hour under laboratory conditions for which diffusion distances are on the scale of the sample size (Dieckmann and Schmalzried, 1986; Mackwell et al., 1988; Ricoult and Kohlstedt, 1985; Schmalzried, 1981, pp. 93–100; Schmalzried, 1995, pp. 117–123; Wanamaker, 1994; Yurek and Schmalzried, 1974). Point defect concentrations respond even more quickly to changes in temperature and pressure for which the appropriate diffusion length is the distance between the sites of repeatable growth, which serve as sources and sinks for point defects (Schmalzried, 1981, pp. 93–96; Schmalzried, 1995, pp. 10–12).

The concentration of vacancies in a mineral will differ from one sublattice to the next. In a system composed of Me = (Mg, Fe), Si, and O, the concentration of vacancies on the Me sublattice is generally several orders of magnitude larger than the concentrations on the Si and O sublattices, that is, $[V_{Me}^{//}] \gg [V_O^\bullet], [V_{Si}^{//}]$ (e.g., Nakamura and Schmalzried, 1983, 1984; Tsai and Dieckmann, 2002). As a result, $D_{Me} \gg D_O, D_{Si}$.

For deformation by diffusion creep or dislocation climb processes, the flux of ions directly enters expressions for the strain rate. The deformation rate is calculated from analyses of the flux of ions between regions experiencing different stress states, such as between grain boundaries in a rock that are oriented normal to and those that are oriented parallel to the maximum principal stress. In an ionic solid, the fluxes of all of the constituent ions must be coupled in order to maintain stoichiometry (Dimos et al., 1988; Gordon, 1973; Jaoul, 1990; Ruoff, 1965; Ready, 1966; Schmalzried, 1995, pp. 345–346). As a consequence, the creep rate of a monomineral rock is controlled by the rate of diffusion of the slowest-diffusing ion.

In the case of olivine, Me_2SiO_4 , for diffusion along parallel paths (i.e., one-dimensional diffusion), the fluxes of Me^{2+} , Si^{4+} , and O^{2-} are given by (e.g., Schmalzried, 1981, p. 63; Schmalzried, 1995, pp. 78–82)

$$j_{Me^{2+}} = -\frac{D_{Me}C_{Me}}{RT} \frac{\partial \eta_{Me^{2+}}}{\partial \xi} = -\frac{D_{Me}C_{Me}}{RT} \left(\frac{\partial \mu_{Me^{2+}}}{\partial \xi} + 2F \frac{\partial \varphi}{\partial \xi} \right) \quad [17a]$$

$$j_{Si^{4+}} = -\frac{D_{Si}C_{Si}}{RT} \frac{\partial \eta_{Si^{4+}}}{\partial \xi} = -\frac{D_{Si}C_{Si}}{RT} \left(\frac{\partial \mu_{Si^{4+}}}{\partial \xi} + 4F \frac{\partial \varphi}{\partial \xi} \right) \quad [17b]$$

and

$$j_{O^{2-}} = -\frac{D_O C_O}{RT} \frac{\partial \eta_{O^{2-}}}{\partial \xi} = -\frac{D_O C_O}{RT} \left(\frac{\partial \mu_{O^{2-}}}{\partial \xi} - 2F \frac{\partial \varphi}{\partial \xi} \right) \quad [17c]$$

where j is the flux, D the self-diffusivity, C the concentration, and η the electrochemical potential of the appropriate ionic species. In eqn [17], ξ is a spatial variable. The electrochemical

Table 1 Dependence of point defect concentrations on oxygen fugacity and water fugacity, expressed as the exponents p and q in the relationship $[] \propto f_{O_2}^p f_{H_2O}^q$, for several charge neutrality conditions for MeO

Charge neutrality	$Me_{Me}^\bullet$	$V_{Me}^{//}$	$V_O^\bullet$	$iMe_{Me}^\bullet - V_{Me}^{//}$	$(OH)_O^\bullet$	$i(OH)_O^\bullet - V_{Me}^{//}$
$[Me_{Me}^\bullet] = 2[V_{Me}^{//}]$	1/6, 0	1/6, 0	−1/6, 0	1/3, 0	−1/12, 1/2	1/12, 1/2
$[(OH)_O^\bullet] = 2[V_{Me}^{//}]$	1/4, −1/6	0, 1/3	0, −1/3	1/4, 1/6	0, 1/3	0, 2/3
$[Me_{Me}^\bullet] = [(OH)_O^\bullet - V_{Me}^{//}]$	1/8, 1/4	1/4, −1/2	−1/4, 1/2	3/8, −1/4	−1/8, 3/4	1/8, 1/4
$[(OH)_O^\bullet] = [i(OH)_O^\bullet - V_{Me}^{//}]$	1/4, 0	0, 0	0, 0	1/4, 0	0, 1/2	0, 1/2

potentials for the various ions are written in terms of the chemical potential, μ , and the electric potential, φ , as (e.g., Schmalzried, 1981, p. 63)

$$\eta = \mu + zF\varphi \quad [18]$$

where z is the charge on the ion and F is the Faraday constant. To maintain stoichiometry during diffusion-controlled creep in which transport of entire lattice molecules must occur between sites of repeatable growth such as dislocations and grain boundaries, the flux coupling condition is

$$\frac{j_{\text{Me}^{2+}}}{C_{\text{Me}}} = \frac{j_{\text{Si}^{4+}}}{C_{\text{Si}}} = \frac{j_{\text{O}^{2-}}}{C_{\text{O}}} \quad [19a]$$

Equation [19a] applies specifically to the case in which all of the ions diffuse along a single path or parallel paths; the more general case in which diffusion occurs along multiple paths (e.g., along grain boundaries and through grain interiors) is treated in Dimos et al. (1988; see also Kohlstedt, 2006).

The flux coupling equation provides a means of eliminating the $\partial\varphi/\partial\xi$ term from the flux equations. The flux coupling condition for olivine in eqn [19a] can be rewritten as

$$2j_{\text{Me}^{2+}} = 4j_{\text{Si}^{4+}} = j_{\text{O}^{2-}} \quad [19b]$$

Then, since $D_{\text{Me}} \gg D_{\text{O}} > D_{\text{Si}}$, the approximation

$$\frac{\partial\eta_{\text{Me}^{2+}}}{\partial\xi} = \frac{\partial\mu_{\text{Me}^{2+}}}{\partial\xi} + 2F\frac{\partial\varphi}{\partial\xi} \approx 0 \quad [20a]$$

that is

$$2F\frac{\partial\varphi}{\partial\xi} \approx -\frac{\partial\mu_{\text{Me}^{2+}}}{\partial\xi} \quad [20b]$$

must hold in order to satisfy eqn [19b]. Using the implicit assumption of local thermodynamic equilibrium, the chemical potentials of the ions can be written in terms of the chemical potentials of the oxides as

$$\mu_{\text{Me}^{2+}} + \mu_{\text{O}^{2-}} = \mu_{\text{MeO}} \quad [21a]$$

and

$$\mu_{\text{Si}^{4+}} + 2\mu_{\text{O}^{2-}} = \mu_{\text{SiO}_2} \quad [21b]$$

Combining eqn [19b] with eqns [17a], [17b], [20b], [21a], and [21b], leads to the relation

$$D_{\text{Si}} \frac{\partial\mu_{\text{SiO}_2}}{\partial\xi} = (D_{\text{O}} + 2D_{\text{Si}}) \frac{\partial\mu_{\text{MeO}}}{\partial\xi} \quad [22]$$

Also, the flux of Si^{4+} , the slowest ionic species, becomes

$$j_{\text{Si}^{4+}} = -\frac{C_{\text{Si}}D_{\text{Si}}}{RT} \left(\frac{\partial\mu_{\text{SiO}_2}}{\partial\xi} - 2\frac{\partial\mu_{\text{MeO}}}{\partial\xi} \right) \quad [23a]$$

Since the chemical potential of olivine is

$$\mu_{\text{Me}_2\text{SiO}_4} = 2\mu_{\text{MeO}} + \mu_{\text{SiO}_2} \quad [24]$$

the flux of Si^{4+} can be rewritten as

$$j_{\text{Si}^{4+}} = -\frac{C_{\text{Si}}D_{\text{Si}}}{RT} \frac{D_{\text{O}}}{D_{\text{O}} + 4D_{\text{Si}}} \frac{\partial\mu_{\text{Me}_2\text{SiO}_4}}{\partial\xi} \quad [23b]$$

The chemical potential of olivine contains an activity, a , term and a stress, σ , term such that

$$\frac{\partial\mu_{\text{Me}_2\text{SiO}_4}}{\partial\xi} = RT \frac{\partial \ln a_{\text{Me}_2\text{SiO}_4}}{\partial\xi} - V_{\text{Me}_2\text{SiO}_4} \frac{\partial\sigma}{\partial\xi} \quad [25a]$$

where $V_{\text{Me}_2\text{SiO}_4}$ is the molar volume of olivine (e.g., Dimos et al., 1988; Gordon, 1973; Ready, 1966; Schmalzried, 1995, p. 334). The first term on the right-hand side of eqn [25a] can be expressed in terms of the gradient in the concentration of vacancies on the Me sublattice (Dimos et al., 1988; Jaoul, 1990; Kohlstedt, 2006) as

$$\begin{aligned} RT \frac{\partial \ln a_{\text{Me}_2\text{SiO}_4}}{\partial\xi} &\approx -2RT \frac{\partial \left[\frac{V_{\text{Me}}}{V_{\text{Me}}} \right]}{\partial\xi} \\ &\approx -2 \left[\left(\frac{V_{\text{Me}}}{V_{\text{Me}}} \right)^0 \right] V_{\text{Me}_2\text{SiO}_4} \frac{\partial\sigma}{\partial\xi} \end{aligned} \quad [26]$$

where $[(V_{\text{Me}}/V_{\text{Me}})^0]$ is the concentration of Me vacancies under hydrostatic stress conditions. The gradient in the concentration in metal vacancies results from the gradient in normal stress between sources for vacancies (regions of minimum compressive stress) and sinks for vacancies (regions of maximum compressive stress). Since $[(V_{\text{Me}}/V_{\text{Me}})^0]$ is small, $<10^{-3}$, the second term in eqn [25a] dominates such that

$$\frac{\partial\mu_{\text{Me}_2\text{SiO}_4}}{\partial\xi} \approx -V_{\text{Me}_2\text{SiO}_4} \frac{\partial\sigma}{\partial\xi} \quad [25b]$$

Therefore,

$$j_{\text{Si}^{4+}} = \frac{C_{\text{Si}}D_{\text{Si}}}{RT} \frac{D_{\text{O}}}{D_{\text{O}} + 4D_{\text{Si}}} V_{\text{Me}_2\text{SiO}_4} \frac{\partial\sigma}{\partial\xi} \quad [27a]$$

and if $D_{\text{O}} \gg D_{\text{Si}}$,

$$j_{\text{Si}^{4+}} = \frac{C_{\text{Si}}D_{\text{Si}}}{RT} V_{\text{Me}_2\text{SiO}_4} \frac{\partial\sigma}{\partial\xi} \quad [27b]$$

2.18.2.2 Line Defects: Structure and Dynamics

Dislocations are line defects that separate regions of a crystal that have slipped from those that have not slipped. Their motion by glide and climb is central to the deformation of most crystalline solids, much like point defects are essential for diffusion. Unlike point defects, dislocations are not equilibrium defects. While the change in enthalpy associated with the formation of a dislocation is quite large, the change in entropy is relatively small. In a simplistic analogy, the former might be considered equal to the change in enthalpy due to the formation of N vacancies, where the vacancies form a row of the same length as the dislocation line. In contrast, the change in entropy resulting from the formation of N vacancies constrained to lie along a line will be significantly less than that associated with the formation of N vacancies randomly distributed in a crystal. The result is that, at equilibrium, a crystal is expected to be dislocation-free (Devereux, 1983, pp. 368–372).

A dislocation is characterized by two vector quantities: its line direction, $\mathcal{L}$, which defines the direction of the dislocation at each point along its length, and a displacement or Burgers vector, $\mathbf{b}$, which defines the displacement of the lattice produced as the dislocation moves through a crystal. For a dislocation loop such as that illustrated in Figure 1, the tangential line direction changes from one point to the next along

the loop, while the Burgers vector is the same at every point. Regions along the dislocation loop for which $\mathbf{b}$ is perpendicular to $\mathcal{L}$ are termed edge segments, while regions for which $\mathbf{b}$ is parallel to $\mathcal{L}$ are termed screw segments. Regions of a dislocation for which $\mathbf{b}$ and $\mathcal{L}$ are neither perpendicular nor parallel are referred to as mixed segments.

Movement of a dislocation can take place by glide and climb. An edge dislocation can move in one of two ways. If an edge dislocation moves in the glide plane defined by $\mathbf{b} \times \mathcal{L}$, its motion is conservative. In contrast, if an edge dislocation moves normal to its glide plane, the process is nonconservative in that lattice molecules are added to or taken away from the dislocation line by diffusion such that the dislocation climbs out of its glide plane. A screw dislocation does not have a specific glide plane since $\mathbf{b}$ and $\mathcal{L}$ are parallel to each other. Hence, a screw dislocation generally glides on the plane that offers least resistance to its motion. If it encounters an obstacle to its movement, a screw dislocation can cross slip off of its original glide plane onto a parallel glide plane in order to continue moving. A dislocation must always move in a direction perpendicular to its line direction. The displacement resulting from glide of an edge dislocation is thus parallel to the direction of dislocation glide, while the displacement resulting from movement of a screw dislocation is perpendicular to its direction of motion defined by the velocity vector, $\mathbf{v}$, as illustrated in Figure 2. Finally, a slip system is

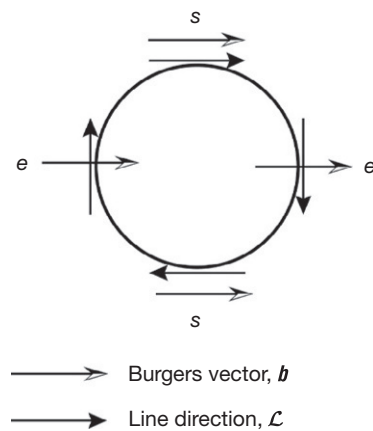


Figure 1 Sketch of dislocation loop indicating the directions of the Burgers vector, $\mathbf{b}$, and of the dislocation line, $\mathcal{L}$, at four points along the loop. The edge and screw segments of the dislocation loop are denoted by e and s , respectively.

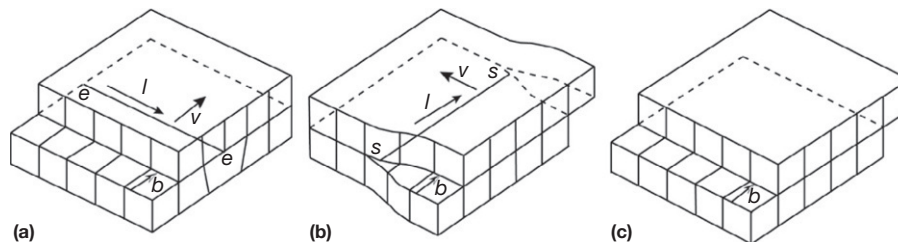


Figure 2 Sketch illustrating that (a) the movement of an edge dislocation, e , and (b) the movement of a screw dislocation, s , with the same Burgers vector (c) produce the same displacement of the upper half of a crystal relative to the lower half. Modified from Kelly A and Groves GW (1970) *Crystallography and Crystal Defects*. Addison-Wesley Publishing Company, p. 199.

defined for a dislocation by the combination of a unit vector normal to the slip plane, $\mathbf{n}$, and $\mathbf{b}$. As an example, important slip systems in clinopyroxene include $\{110\}\langle 1\bar{1}0\rangle$, $\{110\}[001]$, and $(100)[001]$ (Bystrycky and Mackwell, 2001). Slip systems in olivine include $(010)[100]$, $(001)[100]$, $(100)[001]$, and $(010)[001]$ with the dominate slip system determined by stress, and water concentration as well as pressure and temperature (Carter and Avé Lallemant, 1970; Castelnau et al., 2010; Durinck et al., 2005; Jung and Karato, 2001; Mainprice et al., 2005; Raterron et al., 2012).

To the first order, dislocations with short displacement vectors are preferred over those with longer displacement vectors since the energy per unit length of a dislocation, E_{disl} , is proportional to the square of the Burgers vector. For an edge dislocation in an elastically isotropic material (Weertman and Weertman, 1992, pp. 45–52),

$$E_{\text{disl}} = \frac{Gb^2}{4\pi(1-\nu)} \ln \frac{r}{r_c} \quad [28]$$

where G is the shear modulus, r is the mean spacing between dislocations, and r_c is the radius of the dislocation core. In eqn [28], the contribution of the core of the dislocation to the elastic strain energy has been neglected. For elastically anisotropic materials, the full matrix of elastic constants must be considered, as discussed in detail by Hirth and Lothe (1968, pp. 398–440).

Slip generally occurs on the closest packed plane that contains $\mathbf{b}$, that is, the most widely separated planes and thus, in general, the most weakly bonded planes. In olivine, $||100|| < ||001|| < ||010||$ suggesting that $\mathbf{b} = [100]$ should dominate. However, plastic deformation of a polycrystalline material cannot proceed without opening up void space if only one or two independent slip systems operate. Homogeneous plastic deformation of a rock requires dislocation glide on five independent slip systems, a condition known as the von Mises criterion (von Mises, 1928), or glide and climb on three independent slip systems (Groves and Kelly, 1969). Plastic deformation can occur without fracture with glide on four independent slip systems if deformation is allowed to be heterogeneous (Hutchinson, 1976). Processes such as grain-boundary sliding, ionic diffusion, and twinning can also relax the von Mises criterion.

Glide and climb of dislocations involve steps along the dislocation line: steps that lie in the glide plane, called kinks, facilitate glide and steps that are out of the glide plane, called jogs, and facilitate climb.

Dislocations interact with one another and with an applied stress field through the stress field that arises due to the elastic distortion caused by the presence of each dislocation. The stress fields associated with edge and screw dislocations in elastically isotropic and elastically anisotropic media are derived in Hirth and Lothe (1968, pp. 398–440) and in Weertman and Weertman (1992, pp. 22–41). The force on a dislocation is then calculated using the Peach–Koehler equation (Peach and Koehler, 1950). In its simplest form, the force per unit length, f , on a dislocation is

$$f = \sigma b \quad [29]$$

where the stress σ arises, for example, from a neighboring dislocation or an external force.

2.18.2.3 Planar Defects: Structure and Energy

Planar defects include twin boundaries, stacking faults, grain boundaries, and interphase boundaries. The emphasis in this chapter is on grain boundaries and interphase boundaries, because of the important role of these two types of interfaces in plastic deformation.

If the misorientation across a grain boundary is not too large, say $<15^\circ$ (i.e., a low-angle boundary), the interface can be constructed from a periodic array of dislocations. A low-angle tilt boundary consists of a series of parallel edge dislocation, as illustrated schematically in Figure 3 and imaged in Figure 4. In the case of a low-angle tilt boundary, the spacing between dislocations, h , can be expressed in terms of the misorientation angle, ϑ , across the boundary as

$$h = \frac{b}{2 \sin(\vartheta/2)} \quad [30a]$$

For a small misorientation, the misorientation angle can be approximated by

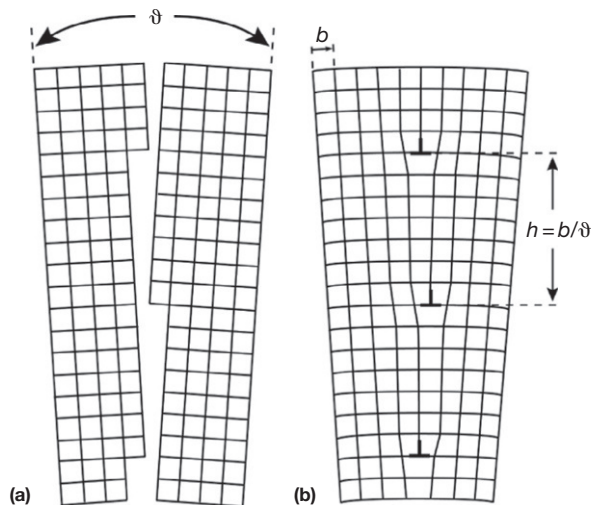


Figure 3 Sketch of a low-angle tilt boundary formed by a series of periodically spaced edge dislocations, which are denoted by the inverted 'T' symbols. Modified from Read Jr WT (1953) *Dislocations in Crystals*. McGraw-Hill Book Company, New York, p. 157.

$$\vartheta \approx \frac{b}{h} \quad [30b]$$

Starting with eqn [28], the elastic strain energy per unit area of a low-angle tilt boundary can then be derived as (Read and Shockley, 1950)

$$E_{\text{tilt}} = \frac{Gb^2}{4\pi(1-\nu)} \frac{\vartheta}{b} (A - \ln \vartheta) \quad [31]$$

where parameter A accounts for the fraction of the elastic strain energy associated with the cores of the dislocations. Once the cores of the dislocations in a tilt boundary begin to overlap, this simple description of a grain boundary breaks down.

A low-angle twist boundary requires two, generally orthogonal, sets of screw dislocations. The elastic energy per unit area for a low-angle twist boundary is similar to that for a low-angle tilt boundary. A sketch of the atomic structure of a low-angle twist boundary formed by rotating the lattices of two grains relative to each other through an angle ϑ , thus forming orthogonal sets of dislocations, is presented in Figure 5. A transmission electron micrograph of a twist boundary is shown in Figure 6.

As illustrated in Figure 7, grain-boundary energy increases rapidly with increasing ϑ , as described by eqn [31], up to $\vartheta \approx 20^\circ$. At larger values of ϑ , grain-boundary energy is approximately constant except for a few minima that occur at specific orientations. Other than twin boundaries, these minima occur at orientations for which a significant fraction of the lattice points in the two neighboring grains are nearly coincident (Chan and Balluffi, 1985, 1986). A simple example of this coincidence structure illustrating the type of periodicity that can be present in specific grain boundaries is shown in Figure 8 for a twist boundary.

Grain and interphase boundaries influence the physical properties of rocks in several important ways. First, grain-boundary sliding provides a mechanism for producing strain in response to an applied differential stress. Grain-boundary sliding takes place by the movement of grain-boundary dislocations. As discussed in the next section, grain-boundary sliding is an essential part of diffusion creep (Raj and Ashby, 1971). Grain-boundary sliding can also be important during deformation in which dislocation glide and dislocation climb operate (e.g., Langdon, 1994). In this case, lattice dislocations

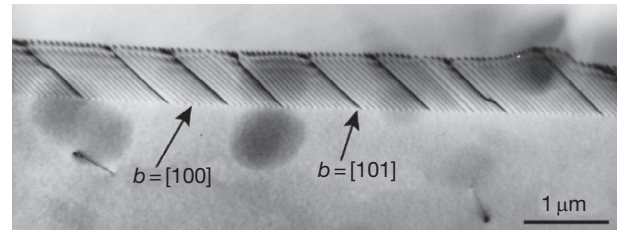


Figure 4 Bright-field transmission electron micrograph of a low-angle tilt boundary in olivine. Two sets of dislocations, one with $b = [100]$ and the other with $b = [101]$, are present in this boundary. The darker $b = [101]$ dislocations are more widely spaced than the lighter, periodically spaced $b = [100]$ dislocations. This image was taken with the diffraction condition $g = (002)$; hence, the $b = [100]$ dislocations exhibit only residual contrast. Modified from Goetze C and Kohlstedt DL (1973) Laboratory study of dislocation climb and diffusion in olivine. *Journal of Geophysical Research* 78: 5961–5971.

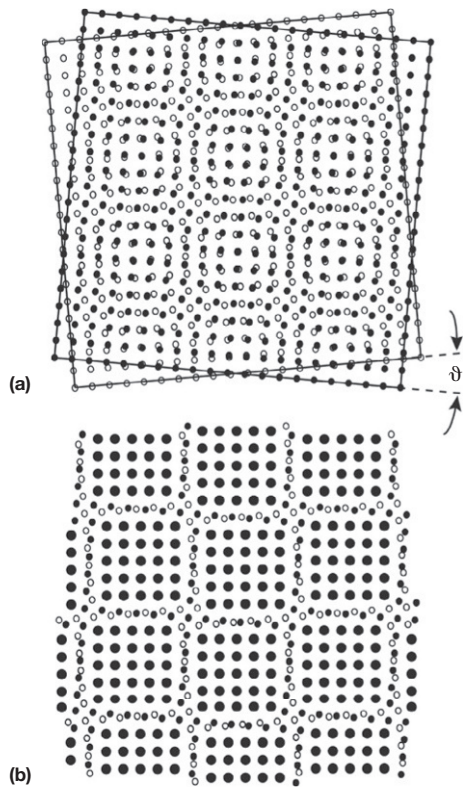


Figure 5 Sketch of atomic configuration for a [001] low-angle twist boundary in a simple cubic lattice with the boundary parallel to the plane of the figure. In this example, $\vartheta \approx 10^\circ$. (a) In the unrelaxed atomic configuration, the open circles represent atoms in the plane just above the boundary, while the closed circles represent the atoms in the plane just below the boundary. (b) In the relaxed atomic configuration, the grains join in regions in which the atomic match is good with two orthogonal sets of screw dislocations located between these regions. Modified from Schmalzried H (1995) *Chemical Kinetics of Solids*. VCH Publishers, New York, p. 51.

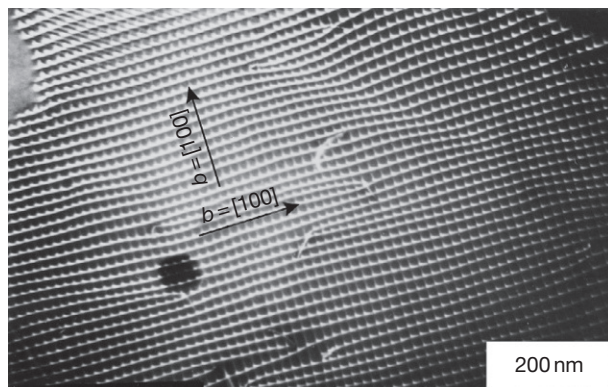


Figure 6 Dark-field transmission electron micrograph of two orthogonal sets of screw dislocations, one with $b = [100]$ and the other with $b = [001]$, forming a low-angle twist boundary in the (010) plane of olivine. The boundary is very nearly parallel to the plane of the figure. Modified from Ricoult DL and Kohlstedt DL (1983a) Structural width of low-angle grain boundaries in olivine. *Physics and Chemistry of Minerals*, 9: 133–138; see also Ricoult and Kohlstedt (1983b).

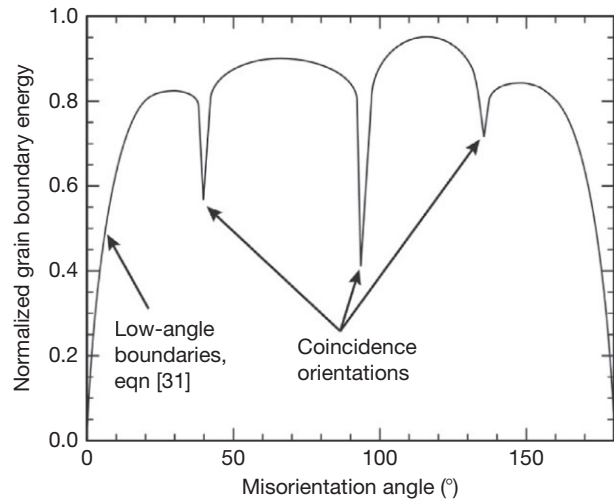


Figure 7 Sketch of normalized grain-boundary energy versus misorientation angle illustrating the energy minima that arise when the two neighboring grains are oriented such that a significant fraction of lattice sites are coincident, such as illustrated in Figure 8.

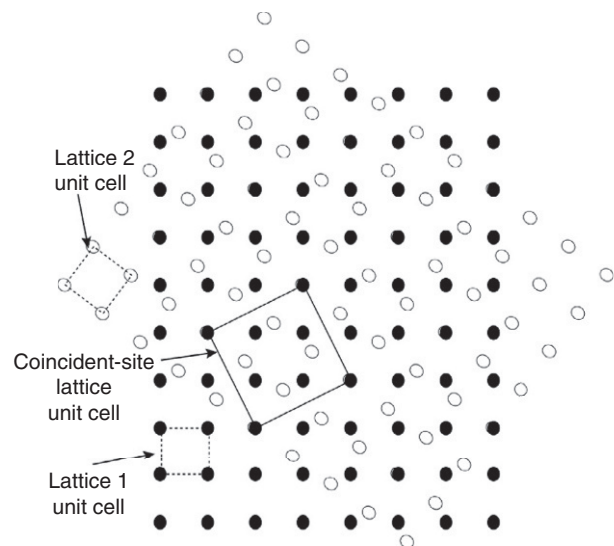


Figure 8 Sketch of lattice sites in two simple cubic grains that have been rotated relative to each other by $\sim 53^\circ$. At this orientation, a fraction of the lattice sites from the two grains coincide forming a coincident-site lattice with a unit cell that is larger than those of the two adjoining grains. Open circles represent atoms in the plane just above the boundary, while the closed circles represent the atoms in the plane just below the boundary.

can dissociate and enter grain boundaries resulting in enhanced or stimulated grain-boundary sliding (Pshenichnyuk et al., 1998). As discussed later in the text, grain-boundary sliding often provides an additional mechanism of deformation and can be particularly important in rocks composed of minerals with fewer than five independent slip systems.

Second, grain boundaries migrate in response to a difference in dislocation density between neighboring grains. As expressed in eqn [28], each dislocation introduces elastic strain

energy into a crystalline grain. If during deformation the dislocation density becomes higher in one grain than in the next grain, a thermodynamic driving force exists that can cause the grain boundary to migrate toward the region of higher dislocation density, absorbing lattice dislocations into the grain boundary, thus reducing the stored elastic strain energy. The dislocation-free region left in the wake of the migrating boundary will deform more easily than neighboring areas in which glide is slowed by dislocation–dislocation interactions.

Third, grain boundaries are short-circuit paths for diffusion. The rate of diffusion along a grain boundary is in general several orders of magnitude faster than through a grain interior (Shewmon, 1983, pp. 164–175). Thus, even though the cross-sectional area of a grain boundary is small relative to that of the grain itself, the flux of ions passing through a grain boundary can be significant. The result is that, in the diffusion creep regime, grain-boundary diffusion is often the primary mechanism for deformation. It should also be noted that grain boundaries provide storage sites for elements that, due to size or charge, are incompatible in the grain interior (Hiraga and Kohlstedt, 2007; Hiraga et al., 2003, 2004, 2007). The presence of incompatible elements at grain and interphase boundaries perturbs the structure and the local charge state of the boundary, which in turn can affect diffusion kinetics (Mishin and Herzig, 1999).

2.18.3 Mechanisms of Deformation and Constitutive Equations

The mechanism of deformation that dominates the plastic deformation of a rock depends both on the properties of the rock such as grain size, d , and phase content, Φ , and on the thermodynamic parameters such as temperature, pressure, P , water fugacity, $f_{\text{H}_2\text{O}}$, and component (oxide) activity, a_{ox} . The dependence of strain rate, $\dot{\epsilon}$, on these quantities can be expressed in a general constitutive equation or flow law as

$$\dot{\epsilon} = \dot{\epsilon}(d, \Phi, T, P, f_{\text{H}_2\text{O}}, a_{\text{ox}}, \dots) \quad [32]$$

Diffusion-controlled creep tends to be important at lower differential stresses in finer-grained rocks. In contrast, dislocation-dominated processes govern flow at higher stresses in coarser-grained rocks. In this section, some of the constitutive equations used to describe flow in the diffusion and dislocation deformation regimes are first introduced. Then, the influence on rheological behavior of two important fluids, water and melt, is discussed. Finally, the development of crystallographic fabrics and their resulting effect on deformation are presented.

2.18.3.1 Constitutive Equations

2.18.3.1.1 Diffusion creep

Diffusion creep can be divided into two regimes, one in which diffusion through the interiors of grains controls the rate of deformation (Herring, 1950; Nabarro, 1948) and the other in which diffusion along grain boundaries governs the rate of deformation (Coble, 1963). The relative importance of these two mechanisms depends primarily on grain size and temperature.

2.18.3.1.1.1 Grain matrix diffusion

The rate of deformation in the Nabarro–Herring creep regime in which diffusion through grain interiors limits the rate of creep is described by the relation (Herring, 1950; Nabarro, 1948)

$$\dot{\epsilon}_{\text{NH}} = \alpha_{\text{NH}} \frac{\sigma V_{\text{m}} D_{\text{gm}}}{RT d^2} \quad [33]$$

where α_{NH} is a geometric term and D_{gm} is the diffusion coefficient for the slowest species diffusing through the grain matrix (gm), that is, the grain interior. Important points to note are that strain rate is linearly proportional to the differential stress, inversely proportional to the square of the grain size, and exponentially dependent on temperature and pressure through the diffusion coefficient since

$$D_{\text{gm}} = D_{\text{gm}}^0 \exp\left(-\frac{\Delta E_{\text{gm}} + P\Delta V_{\text{gm}}}{RT}\right) = D_{\text{gm}}^0 \exp\left(-\frac{\Delta H_{\text{gm}}}{RT}\right) \quad [34]$$

where D_{gm}^0 is a function of the lattice vibration frequency, jump distance, and entropies for formation and migration of vacancies (assuming a vacancy diffusion mechanism) (Shewmon, 1983, pp. 61–62). ΔE_{gm} , ΔV_{gm} , and ΔH_{gm} are the activation energy, activation volume, and activation enthalpy for grain matrix diffusion, respectively; if ionic diffusion occurs via a vacancy mechanism, then each of these three terms is composed of the sum of a contribution for vacancy formation and a contribution for vacancy migration.

2.18.3.1.1.2 Grain-boundary diffusion

A similar expression applies in the Coble creep regime in which the creep rate is limited by diffusion through grain boundaries (Coble, 1963):

$$\dot{\epsilon}_{\text{C}} = \alpha_{\text{C}} \frac{\sigma V_{\text{m}} \delta D_{\text{gb}}}{RT d^3} \quad [35]$$

where α_{C} is a geometric term; δ is the diffusion width of the grain boundary, which is approximately equal to the structural width of ~ 1 nm (e.g., Atkinson, 1985; Carter and Sass, 1981; Ricoult and Kohlstedt, 1983a,b); and D_{gb} is the diffusion coefficient for the slowest species diffusing along grain boundaries. The grain-boundary diffusivity can be expressed as

$$D_{\text{gb}} = D_{\text{gb}}^0 \exp\left(-\frac{\Delta E_{\text{gb}} + P\Delta V_{\text{gb}}}{RT}\right) = D_{\text{gb}}^0 \exp\left(-\frac{\Delta H_{\text{gb}}}{RT}\right) \quad [36]$$

where D_{gb}^0 is similar in nature to D_{gm}^0 in eqn [34] (Schmalzried, 1995, pp. 240–241) and ΔE_{gb} , ΔV_{gb} , and ΔH_{gb} are the activation energy, activation volume, and activation enthalpy for grain-boundary diffusion, respectively. Again, the strain rate increases linearly with increasing differential stress and increases exponentially with inverse temperature while decreasing exponentially with increasing pressure. However, in contrast to the Nabarro–Herring case, strain rate for Coble creep varies inversely as the cube, rather than the square, of the grain size.

Comparison of eqns [33] with [35] reveals the following points: (i) Both creep mechanisms give rise to Newtonian viscous behavior ($\dot{\epsilon} \propto \sigma^1$) with viscosity, $\eta \equiv \sigma/\dot{\epsilon}$, independent of stress. (ii) As long as the grain size is small enough that diffusion creep dominates over dislocation creep, Nabarro–Herring creep ($\dot{\epsilon} \propto 1/d^2$) is more important than Coble creep ($\dot{\epsilon} \propto 1/d^3$) at larger grain sizes. (iii) Nabarro–Herring creep

dominates at higher temperatures and Coble creep at lower temperatures because $\Delta H_{gb} < \Delta H_{gm}$.

The analyses of Nabarro (1948) and Herring (1950) and of Coble (1963) strictly apply to the deformation of a single spherical grain. Subsequent analyses pointed out the necessity of grain-boundary sliding in diffusion creep of polycrystalline materials (Lifshitz, 1963; Raj and Ashby, 1971). The fact that grains tend to be equiaxed in samples deformed in the diffusion creep field indicates that grain-boundary sliding and grain rotation are crucial. The creep process is essentially that of grain-boundary sliding accommodated by diffusion both through grain interiors and along grain boundaries, if grain boundaries are too weak to support shear stress. For this case, $\alpha_{NH} = 14$ and $\alpha_C = 14\pi$. Since grain boundary and grain matrix diffusion are independent/parallel processes, eqns [33] and [35] can be combined to give

$$\dot{\epsilon}_{diff} = 14 \left(\frac{\sigma V_m}{RT} \right) \left(D_{gm} + \frac{\pi \delta D_{gb}}{d} \right) \left(\frac{1}{d^2} \right) \quad [37]$$

In general, this deformation mechanism is referred to simply as diffusion creep. In multicomponent minerals, the rate of diffusion creep is controlled by the slowest species diffusing along its fastest path (grain boundary or grain interior).

2.18.3.1.2 Deformation involving dislocations

As differential stress and/or grain size increases, a transition occurs from diffusion creep to dislocation-dominated deformation. One estimate of the stress required to move from the diffusion creep regime to the dislocation creep regime is based on a calculation of the stress required to operate a Frank–Reed dislocation source, σ_{FR} (Frank and Read, 1950), and thus generate the dislocations necessary to sustain deformation:

$$\sigma_{FR} \approx \frac{2Gb}{L} \quad [38]$$

where L is the length of the dislocation segment operating as the source of new dislocations. If the length of a dislocation line is limited by the grain size, then for $G = 70$ GPa, $b = 0.5$ nm, and $L = d = 10$ μ m, $\sigma_{FR} \approx 7$ MPa.

The strain produced by a single dislocation moving across a grain is very small, thus many dislocations must be generated and move to accomplish a significant amount of deformation. The strain, ϵ , produced in a cubic grain of dimension d by one dislocation moving through the grain is

$$\epsilon = \frac{b}{d} \quad [39]$$

Thus, if $d = 1$ mm, $\epsilon \approx 5 \times 10^{-7}$. Greater strain is achieved by moving a large number of dislocations through the grain. The density of dislocations, ρ , which scales with the magnitude of the applied differential stress, is often written as (Karato, 2008, p. 160; Poirier, 1985, p. 109; Takeuchi and Argon, 1976; Weertman, 1999)

$$\rho \approx \left(\frac{\sigma}{Gb} \right)^2 \quad [40]$$

such that, for olivine, $\rho \approx 10^9$ m⁻² for a differential stress of 1 MPa. The strain produced by this density of dislocations moving a distance x is

$$\epsilon = \rho bx \quad [41]$$

For $x = d$, $\epsilon \approx 5 \times 10^{-4}$, which is still a small value. To produce geologically significant strains, dislocations must be generated, be moved through crystalline grains, and then be removed so that new dislocations can be generated to maintain an approximately constant (steady-state) density of dislocations and keep the deformation process going. If steady-state deformation is attained, then a balance must be achieved, and one step in this series of steps will limit the rate of deformation.

A number of models have been proposed to describe the rate of deformation in terms of applied stress, temperature, pressure, and other thermodynamic and structural variables (e.g., Evans and Kohlstedt, 1995; Poirier, 1985, pp. 94–144). In this chapter, characteristic elements of these models are reviewed in order to provide a framework for examining laboratory-determined deformation data and extrapolating to geologic conditions.

The dependence of the strain rate on differential stress for deformation accomplished by dislocation processes can be examined through the Orowan equation, which is obtained by differentiating eqn [41] with respect to time and noting that in steady state, the dislocation density is independent of time, $\partial \rho / \partial t = 0$ (Orowan, 1940; Poirier, 1985, pp. 62–63):

$$\dot{\epsilon} = \rho b \bar{v} \quad [42]$$

where $\bar{v}$ is the average dislocation velocity. It should be noted, however, that the $\partial \rho / \partial t$ term is critical in the discussions of transient deformation (e.g., deformation immediately following a change in stress). As discussed in reference to eqn [40], the dislocation density is often taken to be proportional to the square of the stress, such that $\dot{\epsilon} \propto \rho \propto \sigma^2$. In addition, an additional dependence of strain rate on differential stress enters through the dislocation velocity term.

In this discussion, dislocation creep is divided into three regimes. As with diffusion creep, the main parameters determining the relative importance of the various dislocation creep mechanisms are differential stress, temperature, pressure, and grain size. First, at high temperature (low stress) and relatively large grain size, all of the strain can be accomplished by glide and climb of dislocations. These conditions define the dislocation creep regime. Second, at high temperature but smaller grain size, grain-boundary sliding operates in conjunction with dislocation processes to produce strain. These conditions define a regime in which dislocation processes are accommodated by grain-boundary sliding or grain-boundary sliding is accommodated by dislocation processes, simply referred to here as the grain-boundary sliding regime. Third, at low temperatures (high stresses), deformation takes place by dislocation glide limited by the intrinsic resistance of the lattice. These conditions delineate the low-temperature plasticity regime.

2.18.3.1.2.1 Dislocation creep

To date, by far the majority of analyses of plastic deformation in geologic materials have used a power-law equation to describe experimental results. A general form of this flow law is

$$\dot{\epsilon} = A \frac{\sigma^n}{d^m} f_{O_2}^p f_{H_2O}^q a_{ox}^r \exp \left(-\frac{Q_{cr}}{RT} \right) \quad [43]$$

where A is a material-dependent parameter and Q_{cr} is the activation energy (strictly, enthalpy) for creep. The power-law form of the creep equation arises by considering the roles of

dislocation climb and grain-boundary sliding in the deformation process.

The potential importance of dislocation climb as the rate-controlling step of high-temperature, steady-state creep was suggested in the early 1950s by Mott (1951, 1953, 1956). Subsequently, several climb-controlled creep models were developed that relate strain rate to differential stress, temperature, and pressure, the latter two through the self-diffusivity (for reviews, see Cannon and Langdon, 1988; Evans and Kohlstedt, 1995; Poirier, 1985, pp. 94–144; Weertman, 1978, 1999). The rate of climb of edge dislocations depends directly on diffusive fluxes of ions (e.g., Hirth and Lothe, 1968, pp. 506–519; Poirier, 1985, pp. 58–62). The justification for emphasizing the importance of climb in high-temperature ($T > 2/3T_m$, where T_m is the melting temperature) deformation of crystalline materials is the one-to-one correlation between the activation energy for creep and the activation energy for self-diffusion of the slowest ionic species, which has been observed for a large number of metallic and ceramic materials (e.g., Dorn, 1956; Evans and Knowles, 1978; Mukerjee et al., 1969; Sherby and Burke, 1967; Takeuchi and Argon, 1976).

Two climb-based models of dislocation creep merit particular attention because of their pioneering contributions in this area and because they incorporate most of the elements found in subsequent models. Weertman (1955, 1957a, b) developed a flow law for steady-state dislocation creep in which dislocation glide produces most of the strain but dislocation climb controls the strain rate. In this model, a dislocation source generates a dislocation loop that expands by gliding until it encounters an obstacle such as a dislocation loop that was generated on a parallel glide plane. The two dislocations interact to form a dipole that prevents further glide until the two dislocations comprising the dipole climb to annihilate one another. Once the dipole is annihilated, the dislocation sources produce new dislocation loops (i.e., dislocation multiplication) to continue the deformation process. If glide is rapid and climb is slow, then the average dislocation velocity is

$$\bar{v} = \frac{\ell_g + \ell_c}{t_g + t_c} \approx \frac{\ell_g}{\ell_c} v_c \quad [44]$$

where $\mathcal{L}_g$ is the glide distance, $\mathcal{L}_c$ is the climb distance, and v_c is the climb velocity (Poirier, 1985, p. 110; Weertman, 1999). The climb velocity, which is determined by diffusion of the slowest atomic/ionic species, is given by the expression (Hirth and Lothe, 1968, pp. 506–519)

$$v_c = 2\pi \frac{\sigma V_m D}{RT} \frac{1}{b \ln(R_o/r_c)} \quad [45]$$

where the average spacing between dislocations, R_o , is usually written in terms of the dislocation density as $R_o \approx 1/\sqrt{\rho}$ and the inner cutoff (core) radius, r_c , is generally set at $r_c \approx b$. A flow law is then obtained by inserting eqns [40] and [45] into the Orowan equation, eqn [42], to yield (Weertman, 1999)

$$\dot{\epsilon} = 2\pi \frac{GV_m}{RT} \left(\frac{\sigma}{G}\right)^3 \frac{D}{b^2} \frac{1}{\ln(G/\sigma)} \frac{\ell_g}{\ell_c} \quad [46]$$

Nabarro (1967) formulated a model for steady-state dislocation creep based solely on dislocation climb. Bardeen-Herring sources (Bardeen and Herring, 1952) generate

dislocations that form a network and continuously climb. Dislocation multiplication occurs by the operation of dislocation sources, thus increasing their density, while climb of dislocations of opposite sign toward one another results in annihilation, thus decreasing their density. A balance between multiplication and annihilation results in steady-state creep described by the flow law (Nabarro, 1967; Nix et al., 1971)

$$\dot{\epsilon} = 2 \frac{GV_m}{RT} \left(\frac{\sigma}{G}\right)^3 \frac{D}{b^2} \frac{1}{\ln(4G/\pi\sigma)} \quad [47]$$

Although the steady-state strain rates obtained from the models developed by Weertman and Nabarro, eqns [46] and [47], respectively, differ in magnitude, these flow laws share fundamental elements. Both yield a cubic dependence of strain rate on differential stress and a linear dependence of strain rate on diffusivity. That is, both result in power-law equations similar to that given in eqn [43] with $m=0$. The exponential dependence of strain rate on temperature enters through D as does at least part of the dependence of strain rate on oxygen and/or water fugacity. In detail, the dependence of diffusivity on fugacity enters through the concentration of the point defects (e.g., vacancies) that enable diffusion of ions, as expressed in eqn [16].

As discussed by Hirth and Lothe (1968, pp. 506–529) and Poirier (1985, pp. 58–62), the climb velocity is directly proportional to the concentration of jogs, c_j , times the migration velocity of jogs, v_j ,

$$v_c = c_j v_j \quad [48]$$

The jog migration velocity is directly proportional to the flux of ions to or from a dislocation and thus directly proportional to the self-diffusion coefficient of the slowest ion. It is usually assumed that dislocations are fully saturated with jogs (i.e., $c_j = 1$) such that the concentration of vacancies remains at local equilibrium along the dislocation line. If the concentration of jogs is significantly below this level (i.e., $c_j \ll 1$), then the jog concentration introduces an extra energy term into the climb velocity, such that the activation energy for climb will be larger than that for self-diffusion of the slowest ion. In addition, as discussed in the succeeding text, if the jog concentration depends on the concentration of other point defects, then c_j may also be a function of thermodynamic parameters such as oxygen fugacity and water fugacity (e.g., Hobbs, 1981, 1983, 1984).

For olivine under anhydrous conditions, the climb-based flow laws in eqns [46] and [47] significantly underpredict the observed rate of deformation for a given set of thermomechanical conditions. Measured laboratory strain rates are a factor of ~ 1000 slower than anticipated from eqn [47], for example, and an unrealistic value of $\mathcal{L}_g/\mathcal{L}_c$ of ~ 200 is needed to bring experiment and theory into agreement (Kohlstedt, 2006). The problem lies in the very slow rate of Si diffusion in olivine, since Si is the slowest-diffusing constituent ionic species and thus rate-controlling. Based on the Si diffusion results of Dohmen et al. (2002) with eqn [45], a dislocation can climb a distance of only ~ 1 nm in a 10 h experiment at an applied stress of 100 MPa at 1500 K. This value is much smaller than that indicated by the kinetics of dislocation recovery (Goetze and Kohlstedt, 1973; Karato and Sato, 1982;

Kohlstedt et al., 1980) and the dislocation microstructures in laboratory-deformed samples (Bai and Kohlstedt, 1992; Durham et al., 1977; Karato et al., 1986). A resolution to this problem was proposed by Hirth and Kohlstedt (2014) in a model that addresses the slow predicted rate of dislocation climb and the difference between the measured and predicted dependence of strain rate on stress ($n = 3.6 \pm 0.2$ vs. $n = 3.0$). These authors emphasize the role of diffusion along dislocation cores (pipe diffusion) as a mechanism that yields faster rates of diffusion and thus of climb. This model introduces an additional dependence of strain rate on dislocation density in the Orowan equation, eqn [42], by scaling the total cross-sectional area for pipe diffusion with the dislocation density (Spingarn et al., 1979). In addition, this model incorporates the measured dependence of dislocation density on applied stress, $\rho \propto \sigma^{1.37}$, rather than the commonly assumed relationship, $\rho \propto \sigma^2$ (eqn [40]). This approach thus directly accounts for the observed rate of dislocation recovery and the measured stress dependence of creep rate. It also helps explain the observation that, for constant oxygen fugacity conditions, the activation energy obtained from dislocation creep experiments, 450 kJ mol^{-1} (Keefner et al., 2011), is smaller than the activation for matrix diffusion of Si, 530 kJ mol^{-1} (Dohmen et al., 2002), as activation energies for short-circuit diffusion are consistently smaller than those for matrix diffusion.

2.18.3.1.2.2 Grain-boundary sliding and migration

Boundaries or interfaces separating neighboring grains often contribute substantially to plastic deformation of rocks. In the diffusion creep regime, sliding along grain and interphase boundaries is an essential aspect of deformation (Raj and Ashby, 1971). Thus, as discussed earlier in the text, diffusion creep might be more descriptively named diffusion-accommodated grain-boundary sliding.

Grain-boundary sliding (gbs) is also important during deformation in which dislocations dominate flow. Grain-boundary sliding has received a great deal of attention in the literature on superplastic deformation, a deformation process in which a solid is deformed (in tension) to very large strains ($\sim 1000\%$ elongation) without failing by necking and subsequent fracture (see, e.g., Ridley, 1995). Based on microstructural analyses, Boullier and Gueguen (1975) argued that superplastic flow is responsible for deformation in at least some mylonites. Schmid et al. (1977) and Goldsby and Kohlstedt (2001) discussed the possibility of superplastic flow in their deformation experiments on limestone and ice, respectively. Recently, Hiraga et al. (2010) conclusively demonstrated superplasticity in fine-grained aggregates of forsterite + periclase and of forsterite + diopside + enstatite by deforming samples in tension to strains of several hundred percent without fracturing. However, as Poirier (1985, p. 204) pointed out, “superplasticity is a behavior, not a definite phenomenon.” Thus, in this chapter, emphasis is given to the coupling between grain-boundary sliding and dislocation glide and/or climb as a deformation process without appealing specifically to the term superplasticity.

In this regime, strain rate varies with differential stress according to a power-law relationship such as the one presented in eqn [43] with $m > 0$ and $n > 1$. This observation immediately implies that grain-boundary sliding cannot be

accommodated simply by diffusion, which would lead to a linear dependence of strain rate on stress (e.g., Ashby and Verrall, 1973). A number of models examine deformation processes involving grain-boundary sliding coupled with dislocation motion. A few of these studies are mentioned here to bring out the key elements of this process, with more extensive lists of references available in Poirier (1985, Section 7.4) and elsewhere (Kaibyshev, 1992; Langdon, 1994, 1995).

Ball and Hutchinson (1969), Mukherjee (1971), and Gifkins (1976, 1978) considered the motion of grain-boundary dislocations impeded by obstacles in the grain boundaries. Stress concentrations that develop at ledges or triple junctions are relieved by the generation of dislocations that then move through the adjoining grains. These dislocations, piled up against neighboring grain boundaries, are removed by climb into the grain boundaries. As these extrinsic dislocations move along grain boundaries, they contribute to grain-boundary sliding. Kaibyshev (2002) in particular emphasized the importance of this excess population of dislocation in grain boundaries due to the interaction of grain boundaries with lattice dislocations. This approach leads to the flow law

$$\dot{\epsilon} = A_{\text{gbs}} \frac{D_{\text{gb}}}{d^2} \frac{GV_m}{RT} \left(\frac{\sigma}{G} \right)^2 \quad [49]$$

where the value of the parameter A_{gbs} , which depends on the details of the grain-boundary sliding process and the dislocation recovery mechanism (see Langdon, 1994), has a value of order 10. This type of analysis is applied to the situation in which a subgrain structure does not build up within the individual grains so that dislocations move relatively freely from one grain boundary, across the grain, to the opposite grain boundary.

If grains contain subgrains, then dislocations that are generated by sliding along a grain boundary glide across the adjoining grain until they encounter a subgrain boundary. The dislocations then climb into the subgrain boundary, interact with dislocations in the subgrain wall, and are annihilated (Langdon, 1994). This type of analysis leads to a flow law of the form

$$\dot{\epsilon} = B_{\text{gbs}} \frac{D_{\text{gm}}}{d^1} \frac{GV_m}{RT} \left(\frac{\sigma}{G} \right)^3 \quad [50]$$

with $B_{\text{gbs}} \approx 1000$. Note that eqns [49] and [50] differ in their dependence on stress (σ^2 vs. σ^3), on grain size ($1/d^2$ vs. $1/d$), and on temperature (Q_{gb} vs. Q_{gm}).

In silicates, evidence for creep involving dislocation-accommodated grain-boundary sliding was identified in deformation data for dry olivine (Hansen et al., 2011; Hirth and Kohlstedt, 1995b, 2003; Wang et al., 2010) and was apparent in the creep results for dry clinopyroxene (Bystricky and Mackwell, 2001) for which a coarse-grained rock is a factor of ~ 10 stronger than a fine-grained sample fabricated from powders prepared from the coarse-grained rock. In rocks composed primarily of highly anisotropic minerals such as olivine, which has only three independent slip systems, grain-boundary sliding can be very important because it relaxes the von Mises criterion of five independent slip systems for homogeneous deformation or four independent slip systems for volume-conserved inhomogeneous deformation. As a

consequence, the strength of coarse-grained dunites lies between those of the stronger two slip systems (Keefner et al., 2011), while the strength of fine-grained dunites for which grain-boundary sliding is a significant deformation mechanism approaches that of the weakest slip system (Hirth and Kohlstedt, 1995b). Interestingly, this dislocation-accommodated grain-boundary sliding regime appears to be absent in olivine-rich rocks deformed under hydrous conditions, possibly because a water (hydrogen)-induced enhancement in ionic diffusivity and thus in dislocation climb velocity provides the extra deformation process required to fulfill the relaxed von Mises criterion (Hirth and Kohlstedt, 2003). As a result, in the hydrous case, the strengths of coarse-grained and fine-grained dunites are both similar to that of the weakest slip system (Mei and Kohlstedt, 2000a).

In addition to their contribution to deformation by producing strain via sliding, grain boundaries facilitate deformation by migrating in response to the strain energy associated with high densities of dislocations within the grains. This dynamic recrystallization process does not itself produce strain; however, it does remove dislocations within grains, resulting in a population of small grains that are, at least initially, free of dislocations. Dislocations generated at grain boundaries can more easily glide across these dislocation-free grains, unimpeded by interactions with other dislocations, than through larger grains that contain high densities of dislocations. In addition, since the contribution of grain-boundary sliding to deformation increases with decreasing grain size as indicated in eqns [49] and [50], grain-boundary sliding can contribute to deformation in regions composed primarily of small grains, thus also enhancing the rate of deformation. Hence, dynamic recrystallization often results in 'strain softening,' a reduction in creep strength with constant-rate, progressive deformation (i.e., increasing strain) of a rock (e.g., de Bresser et al., 2001; Drury, 2005; Platt and Behr, 2011). Dynamic recrystallization can also occur by subgrain rotation by which dislocations are removed from the interiors of grains by addition to low-angle boundaries (e.g., Poirier, 1985, pp. 169–177). As dislocations are added to these (low-angle) subgrain boundaries, the misorientation angle increases until distinct new grains (i.e., high-angle grain boundaries) form. An example of dynamic recrystallization involving both grain-boundary migration and subgrain rotation is presented in Figure 9. Again, the removal of dislocations from within the grains reduces temporarily the number of obstacles to dislocation glide, and the formation of smaller grains makes the operation of grain size-sensitive deformation processes (diffusion creep and dislocation-accommodated grain-boundary sliding) more favorable.

2.18.3.1.2.3 Low-temperature plasticity

At lower temperatures and hence higher stresses, power-law formulations underpredict the observed increase in strain rate with increasing stress. As temperature decreases, diffusion becomes too slow to permit a significant contribution of dislocation climb to the deformation process. The rate of deformation then becomes limited by the ability of dislocations to glide past obstacles. In silicate minerals with a significant component of covalent bonding, dislocations must overcome the resistance imposed by the lattice itself, often referred to as the Peierls barrier (e.g., Frost and Ashby, 1982, pp. 6–9). Motion of dislocations over the Peierls barrier requires the nucleation and

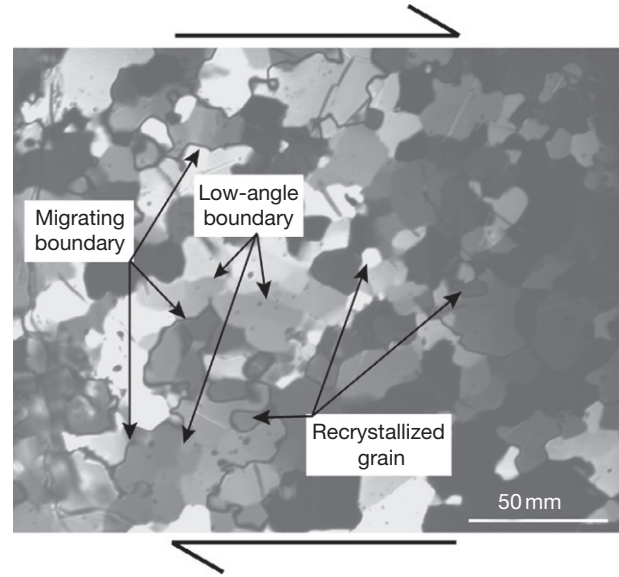


Figure 9 Transmitted light optical micrograph with polarizers crossed of thin section of $(\text{Fe}_{0.5}\text{Mg}_{0.5})_2\text{SiO}_4$ illustrating the process of dynamic recrystallization occurring by both subgrain rotation and grain-boundary migration. Sample was deformed in torsion to a shear strain of $\gamma=4$. Figure courtesy of Y.-H. Zhao.

migration of kinks (steps along dislocation lines that lie in the glide plane), with the nucleation rate of pairs of kinks generally assumed to limit the dislocation velocity (Frost and Ashby, 1982, p. 8). The dislocation velocity is determined by the glide velocity, v_g , and consequently by the kink velocity, v_k :

$$v \approx v_g = c_k v_k \quad [51]$$

where c_k is the concentration of kinks. The activation enthalpy for the nucleation and migration of double kinks, $\Delta H_k(\sigma)$, is a function of differential stress. A detailed analysis for $\Delta F_k(\sigma)$ yields (Frost and Ashby, 1982, p. 8; Kocks et al., 1975, p. 243)

$$\Delta F_k(\sigma) = \Delta F_k^0 \left[1 - \left(\frac{\sigma}{\sigma_p} \right)^r \right]^s \quad [52]$$

where ΔF_k^0 is the Helmholtz free energy of an isolated pair of kinks, σ_p is the Peierls stress, and r and s are model-dependent parameters (Frost and Ashby, 1982, p. 9). From the Orowan equation, eqn [42], the flow law then becomes

$$\dot{\epsilon} = \dot{\epsilon}_p \left(\frac{\sigma}{G} \right)^2 \exp \left\{ - \left\{ \frac{\Delta F_k^0}{RT} \left[1 - \left(\frac{\sigma}{\sigma_p} \right)^r \right]^s \right\} \right\} \quad [53]$$

where $\dot{\epsilon}_p$ is a material-dependent parameter.

2.18.3.1.3 Deformation mechanism maps

An illustrative method for displaying the conditions under which a given deformation mechanism dominates flow is the deformation mechanism map (Frost and Ashby, 1982). At present, olivine is the only mineral for which data exist in the diffusion, dislocation, grain-boundary sliding, and low-temperature plasticity regimes. Four parameters are usually considered when constructing a deformation mechanism map: strain rate, stress, grain size, and temperature. The examination of eqn [32] indicates that other parameters could be

included (e.g., pressure, water fugacity, and melt fraction) depending on the application. Flow parameters for the diffusion and dislocation creep regimes are taken from Hirth and Kohlstedt (2003). Flow parameters for the dislocation-accommodated grain-boundary sliding regime and modified flow parameters for diffusion creep are used from Hansen et al. (2011), while those for the low-temperature plasticity regime are from Mei et al. (2010). The Mei et al. (2010) results, which were obtained in creep experiments in a deformation-DIA apparatus, yield somewhat larger strengths than those obtained from microindentation experiments of Goetze (1978) and Evans and Goetze (1979).

Here, the classical form is first used in which stress is plotted as a function of temperature for a fixed grain size (and fixed pressure, water fugacity, etc.) with strain rate illustrated parametrically. In Figure 10(a) and 10(b), differential stress is plotted as a function of temperature for dunite rocks composed of 10 μm grains and 1000 μm grains, respectively. For a fine-grained rock with $d = 10 \mu\text{m}$ such as might be found in a shear zone (Figure 10(a)), diffusion creep dominates at geologic strain rates, 10^{-15} – 10^{-10} s^{-1} , for stresses below $\sim 100 \text{ MPa}$. At higher stresses, dislocation-accommodated grain-boundary sliding becomes important, and at still higher stresses, low-temperature plasticity dominates. For a coarser-grained rock with $d = 1000 \mu\text{m}$ such as might be expected in the upper mantle (Figure 10(b)), dislocation-accommodated grain-boundary sliding is dominant over more than three orders of magnitude in stress for strain rates relevant to both lithospheric shear zones and asthenospheric flow.

An alternative form of the deformation mechanism map that provides insight into mantle deformation process is obtained by plotting stress as a function of grain size with strain rate again shown parametrically, as illustrated in Figure 11. The greater importance of dislocation-accommodated grain-boundary sliding at the lower temperature (800 $^{\circ}\text{C}$ vs. 1300 $^{\circ}\text{C}$) is clear in this comparison. This behavior reflects the fact that the activation energy for dislocation-accommodated grain-boundary sliding

appears to be smaller than that for dislocation creep, $\sim 445 \text{ kJ mol}^{-1}$ (Hansen et al., 2011) versus $\sim 530 \text{ kJ mol}^{-1}$ (Hirth and Kohlstedt, 2003). Also, the contribution of low-temperature plasticity is, as expected, greater at 800 $^{\circ}\text{C}$. Finally, at 1300 $^{\circ}\text{C}$, the range of grain sizes over which dislocation-accommodated grain-boundary sliding is the dominant mechanism is reduced by an order of magnitude, which primarily serves to increase the grain-size range over which dislocation creep is the dominant mechanism.

2.18.3.2 Role of Fluids in Rock Deformation

Melt and water significantly influence the strength of a rock. If either is present even in small concentration, it profoundly affects rock viscosity.

2.18.3.2.1 Role of melt in rock deformation

The influence of melt on rock viscosity enters constitutive equations in two ways (for reviews, see Kohlstedt, 1992, 2002; Xu et al., 2004). First, melt provides a path along which ions can diffuse more rapidly than they can either through grain interiors or along grain boundaries. Second, since melt does not support shear stresses, for a given applied macroscopic stress, the stress at the grain scale will be locally increased if melt is present.

Both of these contributions to the high-temperature strength of a rock were included in the analysis of Cooper and Kohlstedt (1984, 1986) and Cooper et al. (1989) of the effect of melt on diffusion creep of aggregates composed of a fluid phase plus a solid phase. Such analyses depend critically on the distribution of the melt phase. In this particular model, the melt distribution was assumed to be dictated by surface tension for an isotropic system under a hydrostatic state of stress for which the dihedral angle, θ , is determined by the relative values of the solid-liquid and solid-solid interfacial energies, γ_{sl} and γ_{ss} , respectively:

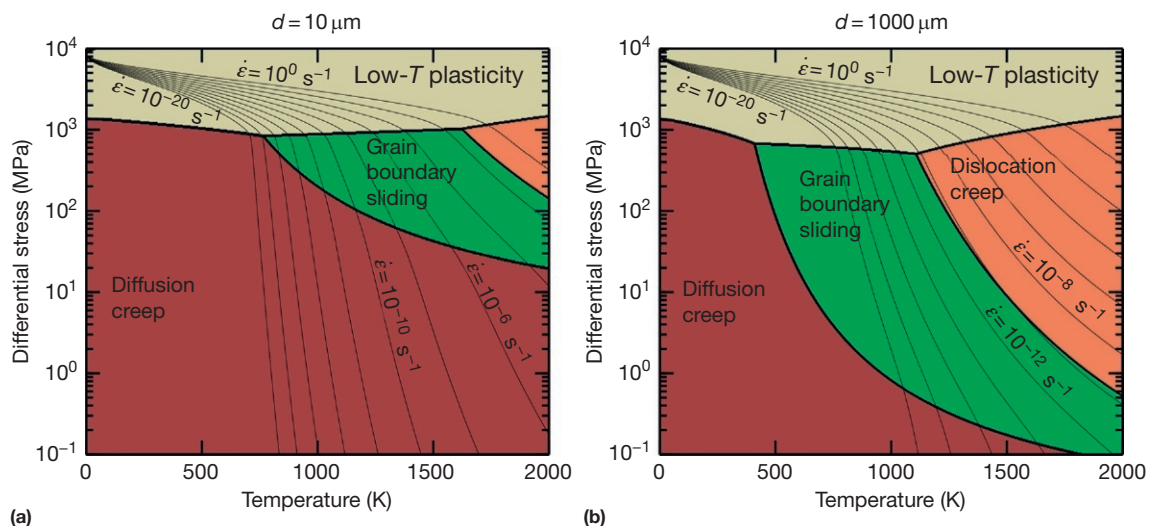


Figure 10 Deformation mechanism maps plotted as differential stress as a function of temperature for dunite with grain sizes of (a) 10 μm and (b) 1000 μm . (a) At the smaller grain size for a strain rate of 10^{-15} s^{-1} , deformation occurs by diffusion creep for stresses up to $\sim 200 \text{ MPa}$ above which deformation is dominated by grain-boundary sliding and then by low-temperature plasticity. (b) At the larger grain size for a strain rate of 10^{-15} s^{-1} , deformation occurs by grain-boundary sliding for a much larger range of stress (0.2–600 MPa).

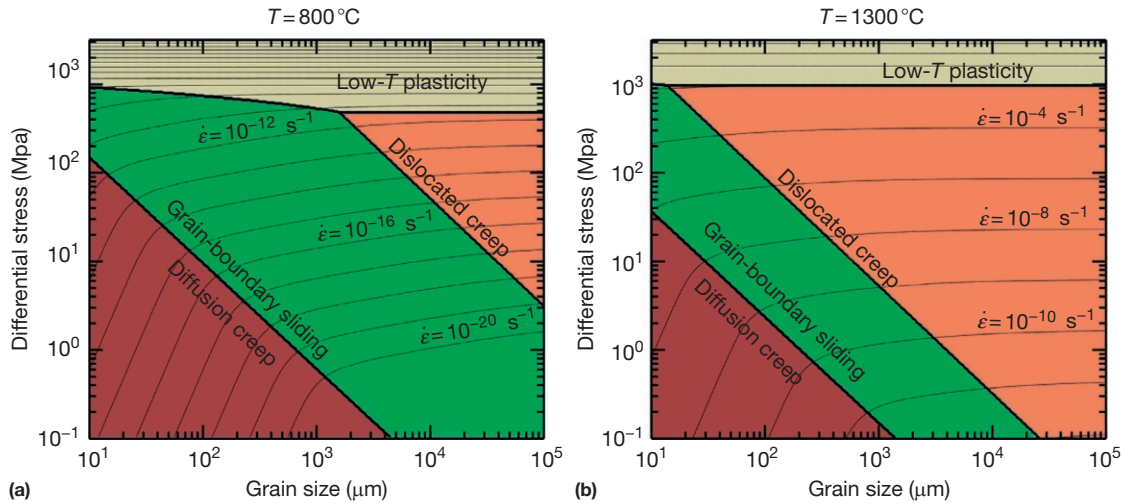


Figure 11 Deformation mechanism maps plotted as differential stress as a function of grain size for dunite at temperatures of (a) 800° and (b) 1300 °C. (a) At the lower temperature for a strain rate of 10^{-15} s^{-1} , deformation occurs by diffusion creep for grain sizes less than $\sim 80 \mu\text{m}$, by grain-boundary sliding at grain sizes between 80 and 10 000 μm , and by dislocation creep at grain sizes larger than 10 000 μm . (b) At a comparable stress for the higher temperature, the boundary between diffusion creep and grain-boundary sliding occurs at a factor of ~ 2 smaller grain size than at the lower temperature, but the boundary between grain-boundary sliding and dislocation creep occurs at a factor of ~ 100 smaller grain size than at a comparable stress for the lower temperature.

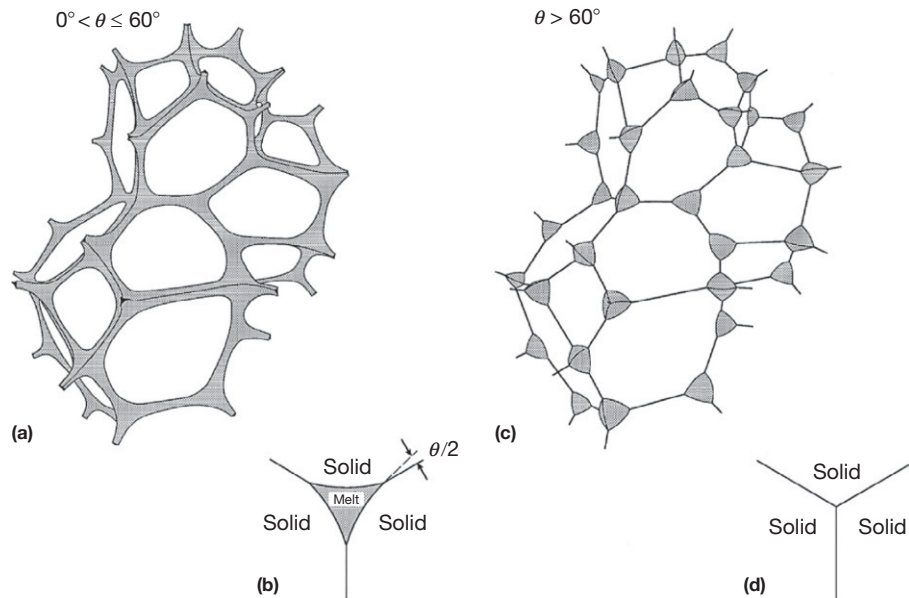


Figure 12 Sketch of melt distribution in a partially molten rock with isotropic interfacial energies. In (a) with $0^\circ < \theta \leq 60^\circ$, melt wets all of the triple junctions and four-grain junctions; (b) cross section through a triple junction midway along a grain edge illustrates the presence of melt. In (c) with $\theta > 60^\circ$, melt is confined to four-grain junctions; (d) cross section through a triple junction midway along a grain edge illustrates the absence of melt. Modified from Riley Jr GN and Kohlstedt DL (1990) An experimental study of melt migration in an olivine–melt system. In: Ryan MP (ed.), *Magma Transport and Storage*. John Wiley & Sons, New York, pp. 77–86.

$$\cos\left(\frac{\theta}{2}\right) = \frac{\gamma_{ss}}{2\gamma_{sl}} \quad [54]$$

For the olivine+MORB case, the average dihedral angle is $\sim 40^\circ$ (i.e., $0 < \theta < 60^\circ$) such that, ideally, melt forms an interconnected network along three-grain junctions and through four-grain corners, such as illustrated in Figure 12. Average values for dihedral angle of $< 60^\circ$ are observed for many rocks composed of silicate minerals plus a silicate melt.

However, as illustrated in Figure 13, for melt fractions greater than ~ 0.05 , the model of Cooper and Kohlstedt (e.g., Cooper and Kohlstedt, 1986) significantly underpredicts the decrease in viscosity measured in experiments on partially molten rocks in the diffusion creep regime (Hirth and Kohlstedt, 1995a; Zimmerman and Kohlstedt, 2004).

One important aspect not taken into account in the previously mentioned analysis is the fact that the wetting

behavior of most partially molten systems is not isotropic (e.g., Cooper and Kohlstedt, 1982). As illustrated in Figure 14, microstructural observations demonstrate that melt wets a fraction of the grain boundaries, behavior not predicted for an isotropic system with $\theta > 0^\circ$. Furthermore, the percentage of grain boundaries wetted by melt increases with increasing melt fraction, ϕ (Hirth and Kohlstedt, 1995b).

To deal with the influence of melt distribution on diffusion creep, Takei and Holtzman (2009a) expressed the viscosity of a partially molten rock in terms of grain-boundary contiguity, φ , a state variable equal to the ratio of grain-boundary area to grain-boundary area plus grain-melt interfacial area. This

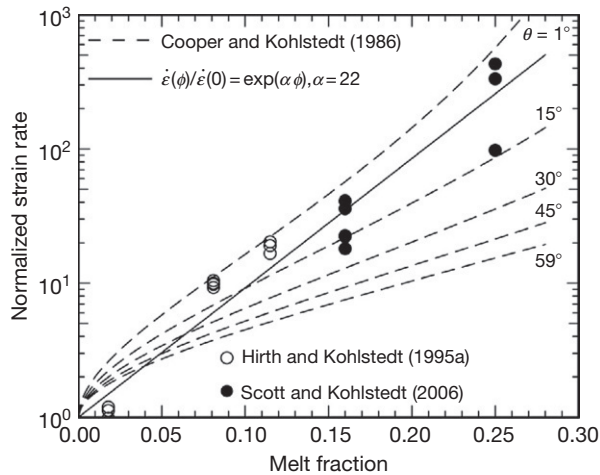


Figure 13 Plot of normalized strain rate, $\dot{\epsilon}(\phi)/\dot{\epsilon}(0)$, versus melt fraction. Circles are the experimentally determined values; for $\phi < 0.15$, data are from Hirth and Kohlstedt (1995a), while for $\phi > 0.15$, data are from Scott and Kohlstedt (2006). Dashed curves are based on the model of Cooper and Kohlstedt (1986) for $1^\circ \leq \theta \leq 59^\circ$. Solid line is a fit to the experimental data to the empirical relationship $\dot{\epsilon}(\phi)/\dot{\epsilon}(0) = \exp(\alpha\phi)$, yielding $\alpha = 22$.

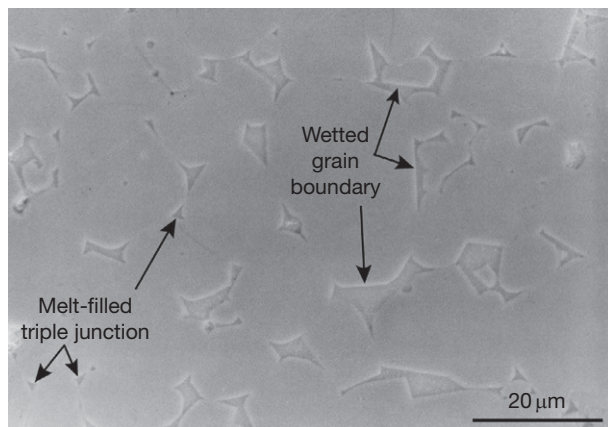


Figure 14 Backscattered scanning electron micrograph of sample of olivine + 5% basalt. Both melt-filled triple junctions and wetted grain boundaries are identified. The presence of wetted grain boundaries demonstrates that the interfacial energies are anisotropic in this system, since melt would be confined to triple junctions in an isotropic system with a similar dihedral angle of $\theta \approx 40^\circ$.

model extends that of Cooper and Kohlstedt (1984, 1986) from two to three dimensions, incorporating the observed anisotropic wetting of grains. The Takei and Holtzman (2009a) analysis expresses the viscosity of a partially molten rock in terms of contiguity and the viscosity of the melt-free material, η_0 , as

$$\eta(\phi) = 0.2\varphi^2\eta_0 = 0.2\left(1 - A\phi^{1/2}\right)^2\eta_0 \quad [55]$$

Contiguity is then written in terms of melt fraction using the semiempirical relationship $\varphi = (1 - A\phi^{1/2})$ with $A = 2.3$. One important result of this model is that it predicts a factor of greater than five decrease in viscosity as melt fraction is increased from 0 to 0.001 (i.e., 0.1% melt). This model yields a good fit to the experimental data on samples of borneol+diphenylamine, an organic binary eutectic system (McCarthy and Takei, 2011), and samples of sol-gel-derived olivine+basaltic melt (Faul and Jackson, 2007). Both materials exhibit the predicted large decrease in viscosity in going from $\phi = 0$ to $\phi = 0.001$, as illustrated in Figure 15 for the organic system.

Experimental determinations of strain rate as a function of melt fraction in both the diffusion creep regime and the dislocation creep regime have been empirically fit to the relation

$$\dot{\epsilon}(\phi) = \dot{\epsilon}(0)\exp(\alpha\phi^r) \quad [56]$$

for melt fractions from near zero to the rheologically critical melt fraction (RCMF) with $r = 1$ for the olivine+basalt system (Kelemen et al., 1997; Mei et al., 2002; Scott and Kohlstedt, 2006) and the borneol plus eutectic melt system (Takei, 2005) and $r = 3$ for a partially molten granitic rock (Rutter and Neuman, 1995; Rutter et al., 2006). This exponential dependence of strain rate on melt fraction is consistent with the dependence of viscosity on melt fraction derived by Takei and Holtzman (2009a) given by eqn [55] for $\phi \geq 0.01$ with $r = 1$ and $\alpha = 23$, as illustrated in Figure 15.

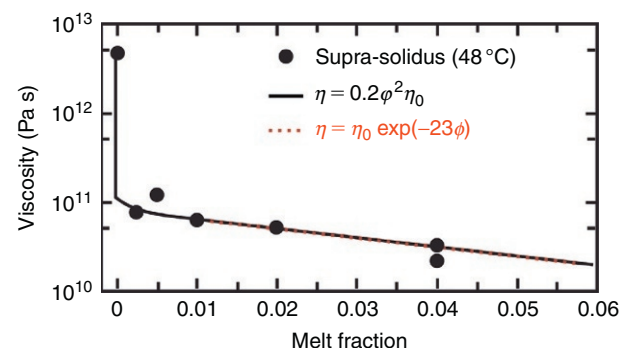


Figure 15 Viscosity as a function of melt fraction for the borneol ($C_{10}H_{18}O$)-diphenylamine ($(C_6H_5)_2NH$) binary eutectic organic system, which has a eutectic temperature of $T_e = 43^\circ C$. The data are well fit by eqn [55], which relate viscosity to melt fraction (Takei and Holtzman, 2009a). At melt fractions greater than ~ 0.01 , the experimental results are also well described by the empirically derived, exponential relationship between viscosity and melt fraction, eqn [56]. Modified from McCarthy C and Takei Y (2011) Anelasticity and viscosity of partially molten rock analog: Toward seismic detection of small quantities of melt. *Geophysical Research Letters* 38: <http://dx.doi.org/10.1029/2011GL048776>.

At least for $\phi \geq 0.01$, melt has a greater influence on viscosity in the dislocation creep regime than in the diffusion creep regime for the olivine + basalt and partially molten lherzolite systems (Mei et al., 2002; Scott and Kohlstedt, 2006; Zimmerman and Kohlstedt, 2004). This point is illustrated in Figure 16 with $\alpha = 21$ in the diffusion creep regime and $\alpha = 32$ in the dislocation creep regime. At melt fractions greater than the RCMF, a partially molten rock behaves as a fluid (melt) containing suspended particles. The Einstein–Roscoe equation (Roscoe, 1952),

$$\eta_{ER}(\phi) = \frac{\mu}{(1.35\phi - 0.35)^{2.5}} \quad [57]$$

which reasonably well describes the viscosity of a system with $\phi > 0.25$ –0.30, is also shown in Figure 16. In eqn [57], μ is the melt viscosity. It is also important to note that the onset of melting will affect grain-boundary chemistry, which will indirectly – but significantly – affect rock viscosity through its influence on the rates of ionic diffusion along grain boundaries (Hiraga et al., 2007; McCarthy and Takei, 2011).

Importantly, not only does a small amount of melt significantly affect rock viscosity, but also, in turn, deformation profoundly influences melt distribution (Holtzman et al., 2003a,b; King et al., 2010; Kohlstedt and Zimmerman, 1996; Kohlstedt et al., 2010; Takei and Holtzman, 2009a, 2009b). The scale and extent of the influence of stress on melt distribution are determined by the compaction length, δ_c (Holtzman et al., 2003a; Stevenson, 1989), where $\delta_c = \sqrt{(k/\mu)(\frac{2}{3}\eta + \zeta)}$ with k the permeability, η the shear viscosity, and ζ the bulk viscosity. For δ_c larger compared to the size of the region (sample) undergoing

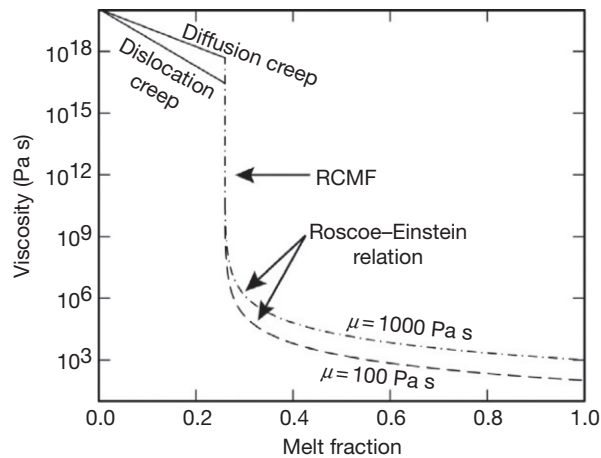


Figure 16 Plot of viscosity of a partially molten rock versus melt fraction for $\phi > 0.01$ illustrating the transition between flow controlled by a framework of solid particles with interstitial melt and flow dominated by melt with suspended particles. At low melt fractions, dislocation creep and diffusion creep are described by eqn [55] with $r = 1$ and $\alpha = 21$ and 32, respectively. At the rheologically critical melt fraction, which marks the transition from solid-like to fluid-like behavior, viscosity plummets rapidly with increasing melt fraction. At higher melt fractions, $\phi > 0.25$ –0.30, the Roscoe–Einstein relation, eqn [56], describes deformation of a mixture of melt with suspended particles. Modified from Scott T and Kohlstedt DL (2006) The effect of large melt fraction on the deformation behavior of peridotite. *Earth and Planetary Science Letters* 246: 177–187.

deformation, melt aligns 15–25° to the shear plane, antithetic to the shear direction (Kohlstedt and Zimmerman, 1996; Zimmerman et al., 1999). An example of stress-driven melt alignment is presented in Figure 17 for the olivine + basalt system. For δ_c smaller than the region of deformation, melt spontaneously segregates into melt-enriched bands, again aligned 15–25° to the shear plane, antithetic to the shear direction (Holtzman et al., 2003a,b; King et al., 2010; Kohlstedt et al., 2010). An example of stress-driven melt segregation is included in Figure 18 for an olivine + basalt + chromite sample. The role of chromite in this sample is to reduce the permeability and thus the compaction length (Holtzman et al., 2003a).

The formation of melt-enriched bands or sheets occurs in partially molten rocks for which viscosity decreases with increasing melt fraction (Stevenson, 1989). In these rocks, the melt-enriched bands develop at a low angle to the shear plane (Figure 18) as a result of the viscous anisotropy produced by stress-driven alignment of melt at the grain scale (Figure 17), that is, microstructural anisotropy (Takei and Holtzman, 2009b; Takei and Katz, 2013). These melt-enriched layers have a significantly lower viscosity than the neighboring melt-depleted regions, thus forming zones of localized deformation (shear zones) that reduce the rock viscosity relative to the viscosity of a partially molten rock in which the melt is homogeneously distributed (Holtzman et al., 2012; King et al., 2010). Melt-enriched layers also act as high-permeability paths for rapid extraction of melt from the mantle (Kelemen and Dick, 1995; Kohlstedt and Holtzman, 2009).

2.18.3.2.2 Role of water in rock deformation

Water weakening of nominally anhydrous silicate minerals was first observed in the mid-1960s in an experimental study of the strength of quartz (Griggs and Blacic, 1965). In these solid-

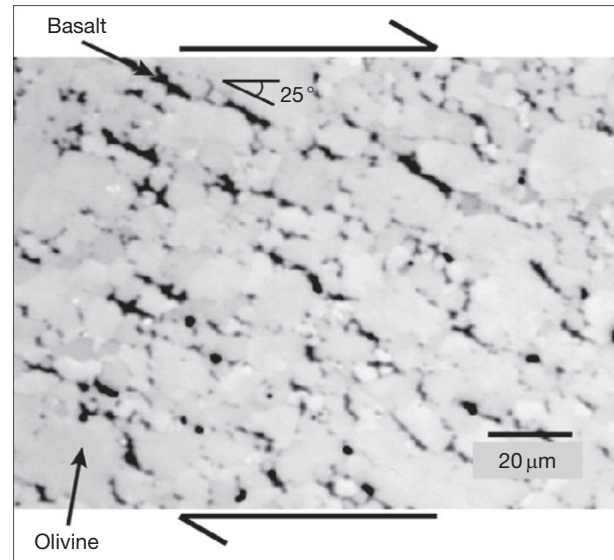


Figure 17 Sample of olivine + 3 vol% MORB deformed in general shear. Melt (black) is aligned at the grain scale 20–25° to the shear plane, antithetic to the shear direction. Olivine grains are light gray. Modified from Kohlstedt DL and Zimmerman ME (1996) Rheology of partially molten mantle rocks. *Annual Review of Earth and Planetary Sciences* 24: 41–62.

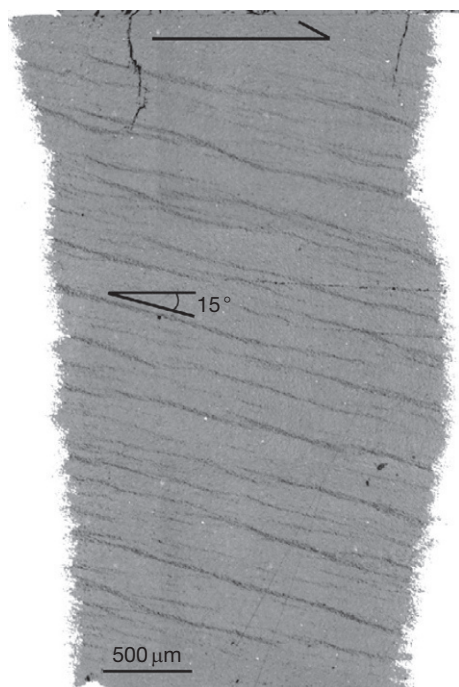


Figure 18 Reflected light photomicrograph of a tangential surface of a sample of olivine (72%), chromite (24%), and basalt (4%) deformed in torsion to an outer-radius shear strain of 1.3 at an outer-radius strain rate of $1.8 \times 10^{-5} \text{ s}^{-1}$ and outer-radius shear stress of 57 MPa. The darker bands trending NW–SE are melt-enriched, containing up to ~20 vol% basalt. The lighter gray regions are melt-depleted, containing < 1 vol% basalt. Two unloading cracks extend from the top dunite piston a short distance into the sample. Modified from King D, Zimmerman ME, and Kohlstedt DL (2010) Stress-driven melt segregation in partially molten olivine-rich rocks deformed in torsion. *Journal of Petrology* 51: 21–42, <http://dx.doi.org/10.1093/petrology/egp062>.

medium deformation experiments, samples deformed with a hydrous confining medium (talc) were weaker than samples deformed with an anhydrous confining medium. Subsequently, water weakening has been reported for other nominally anhydrous minerals (NAMs) including olivine (e.g., Avé Lallemant and Carter, 1970), pyroxene (Avé Lallemant, 1978), and feldspar (e.g., Tullis and Yund, 1980). These first studies of water weakening emphasized the phenomenon. A second generation of experiments focused on the mechanism of water weakening by studying the dependence of viscosity on water fugacity, that is, on the concentration of water-derived point defects (Chen et al., 2006; Karato and Jung, 2003; Kohlstedt et al., 1995; Kronenberg and Tullis, 1984; Mei and Kohlstedt, 2000a,b; Post et al., 1996).

The first model of water or hydrolytic weakening was built on a mechanism in which water hydrolyzes strong Si—O bonds forming weaker Si—OH...OH—Si bonds (Griggs, 1967). Thus, dislocation glide is easier under hydrous conditions than under anhydrous conditions; effectively, the Peierls stress/barrier decreases as Si—O—Si bridges become hydrolyzed. In this analysis, the rate of dislocation glide is limited by the propagation of kinks along dislocations, a process facilitated by the diffusion of water along dislocation cores. Dislocation velocity is then taken to be proportional to the concentration of water (Griggs, 1974).

More recent models of water weakening have emphasized the role of water-derived point defects, particularly hydrogen ions (protons) (Hobbs, 1981, 1983, 1984; Mackwell et al., 1985; Poumellec and Jaoul, 1984). Protons diffuse rapidly in NAMs (for a review, see Ingrin and Skogby, 2000) such as quartz (Kronenberg et al., 1986), olivine (Demouchy and Mackwell, 2003; Kohlstedt and Mackwell, 1998, 1999; Mackwell and Kohlstedt, 1990), and pyroxene (Carpenter Woods et al., 2000; Hercule and Ingrin, 1999; Ingrin et al., 1995; Stalder and Skogby, 2003). Thus, initially dry, millimeter-size samples can be hydrated in high-temperature, high-pressure experiments lasting a few hours or less. The presence of protons in a NAM affects the velocity of a dislocation in two possible ways. First, since protons are charged, a change in the concentration of protons will result in a change in the concentration of all other charged point defects. Hence, the introduction of protons into a NAM will directly affect the concentrations of vacancies and self-interstitials on each ionic sublattice and consequently the rates of diffusion of the constituent ions and the rate of dislocation climb. In addition, extrinsic point defects, specifically water-derived point defects, can affect the concentrations of kinks and jogs along dislocation lines and thus dislocation velocity as expressed in eqns [48] and [51] (Hirsch, 1979, 1981; Hobbs, 1981, 1984). The effect of water-derived point defects on the concentrations of kinks and jogs can enter defect reactions in two ways. First, for minerals containing a transition metal such as Fe (i.e., semi-conducting silicates), the presence of water-derived point defects will affect the concentration of electron holes, $h^\bullet$, which in turn can affect the concentrations of kinks and jogs by ionizing initially neutral jogs (Hirsch, 1979, 1981; Hobbs, 1984). For the case of kinks, a positively charged kink, $k^\bullet$, can be produced from a neutral kink by the reaction



for which the law of mass action yields

$$[k^\bullet] = K_{58} [k^\times] [h^\bullet] \quad [59]$$

The total concentration of kinks then becomes

$$[k^{\text{tot}}] = [k^\times] + [k^\bullet] = [k^\times] (1 + K_{58} [h^\bullet]) \quad [60]$$

where the second term can be much larger than unity and dominate the kink population. The dependence of kink concentration on water (proton) concentration or water fugacity then enters through the concentration of positively charged kinks, thus enhancing the dislocation glide velocity. A similar argument can be used for increasing the concentration of jogs and thus the dislocation climb velocity. While this approach provides one mechanism for increasing dislocation velocity in NAMs, it is not easily extended to minerals such as quartz that do not contain significant concentrations of transition metals. Therefore, a more direct influence of water-derived point defects on kink and jog concentrations needs to be considered. In point defect notation, the addition of protons, $p^\bullet$, to a nominally anhydrous silicate will affect the concentration of kinks through a reaction such as



where the curly brackets, $\{ \}$, indicate the formation of a neutral kink associated with a proton. The application of the law of mass action yields

$$[\{k^{\times} - p^{\bullet}\}^{\bullet}] = K_{61} [k^{\times}] [p^{\bullet}] \quad [62]$$

The total concentration of kinks is then

$$[k^{\text{tot}}] = [k^{\times}] + [\{k^{\times} - p^{\bullet}\}^{\bullet}] = [k^{\times}] (1 + K_{61} [p^{\bullet}]) \quad [63]$$

Again, a similar equation applies for jogs. The dependence of kink and jog concentrations on water concentration/fugacity then comes directly through the dependence of proton concentration on water fugacity.

The high-temperature deformation behaviors of anorthite, clinopyroxene, and olivine deformed in the dislocation creep regime under anhydrous and under hydrous conditions are compared in Figure 19. A similar comparison was made for the diffusion creep regime by Hier-Majumder et al. (2005a). In the dislocation creep regime, the dependence of strain rate on water fugacity has been quantified for olivine (Hirth and Kohlstedt, 2003; Karato and Jung, 2003; Mei and Kohlstedt, 2002b) and for clinopyroxene (Chen et al., 2006). In the case of olivine, strain rate increases as water fugacity to the ~ 1 st power, while in the case of clinopyroxene, strain rate increases as water fugacity to the ~ 3 rd power. In the diffusion creep regime, creep rate increases as water fugacity to the ~ 1 st power for olivine

(Mei and Kohlstedt, 2000a) and to the ~ 1.4 power for clinopyroxene (Hier-Majumder et al., 2005a).

To help assess possible explanations for these observed dependences of strain rate on water fugacity, Table 2 summarizes the relationships between the concentration of various point defects and water fugacity for several charge neutrality conditions for a transition-metal silicate. For olivine under hydrous conditions, the activation energy for dislocation creep of $470\text{--}520 \text{ kJ mol}^{-1}$ (Hirth and Kohlstedt, 2003; Karato and Jung, 2003) is somewhat larger than those for Si and O self-diffusion of 360 and 440 kJ mol^{-1} , respectively (Costa and Chakraborty, 2008). Over the temperature range explored experimentally ($1200\text{--}1350^\circ\text{C}$), the diffusivities of Si and O are of similar magnitude. Thus, if the high-temperature creep of olivine is controlled by dislocation climb limited by the diffusion of the slowest ionic species, it is not clear which species (Si or O) is rate-controlling. Karato and Jung (2003) proposed a model in which creep rates are controlled by dislocation climb with Si diffusing by a vacancy mechanism coupled with positively charged jogs leading to a water fugacity exponent of $q=5/4$ in eqn [43], close to the value that they obtained from their deformation experiments of 1.2 . A water fugacity exponent of $5/4$ is also satisfied by Si diffusing via a vacancy mechanism with the dominate Si vacancy resulting from the defect associate $[(3\text{H})_{\text{Si}}]$ with the charge neutrality condition $[h^{\bullet}] = [H_{\text{Me}}^{\bullet}]$ (see Table 2). In both cases, it is difficult to reconcile the substantial difference between the activation energies for Si self-diffusion and creep.

The situation appears to be equally or possibly more complex for clinopyroxene. The stress exponent is $n=2.7\pm 0.3$, consistent with the climb-controlled creep models discussed in the preceding text. Unfortunately, diffusion data are lacking for comparison with the creep data. The relatively strong dependence of strain rate on water fugacity, $q=3.0\pm 0.6$, in the dislocation creep regime suggests that a simple climb-controlled mechanism may not apply for high-temperature deformation of clinopyroxene (see Table 2). One possible way to reconcile this large value for the water fugacity exponent is as follows: (a) Creep is climb-controlled; (b) charge neutrality condition is given by $[h^{\bullet}] = [H_{\text{Me}}^{\bullet}]$ or by $[p^{\bullet}] = [H_{\text{Me}}^{\bullet}]$; (c) strain rate is limited by Si diffusion by a vacancy mechanism involving the defect associate $\{4p^{\bullet} - V_{\text{Si}}^{\text{vac}}\}^{\times} \equiv (4\text{H})_{\text{Si}}^{\times}$; and (d) dislocations are undersaturated with jogs with the jog concentration dominated by neutral jogs associated with protons, $\{j^{\times} - p^{\bullet}\}^{\bullet}$, as in eqns [62] and [63]. These scenarios yield a water fugacity exponent for strain rate of $2^{3/4}$ and $2^{1/2}$, both within the experimental uncertainty of the measured value. Clearly, diffusion data are critical in order to develop this type of argument more completely.

As is evident from the previously mentioned analysis of high-temperature creep data for olivine and clinopyroxene, unambiguous identification of creep mechanism is difficult, at best. The complication arises because multiple ionic species and defect types are involved, including some of the following: Si, O, Me, vacancies, interstitials, dislocations, jogs, and kinks. At the very least, robust diffusion results are required for all of the constituent ionic species, including not only the magnitude of diffusivity but also the dependence of diffusivity on temperature and water fugacity and on other thermodynamic parameters. Nonetheless, the application of rheological data to

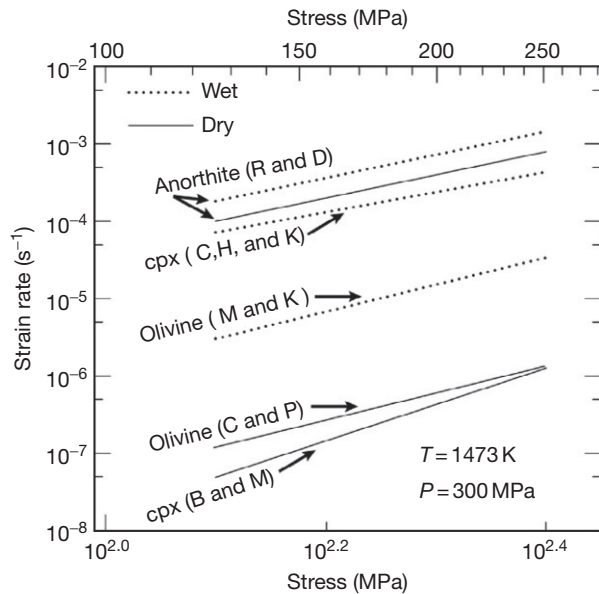


Figure 19 Strain rate versus stress for samples of anorthite, clinopyroxene, and olivine deformed in the dislocation creep regime under anhydrous and hydrous conditions. In each case, samples deformed under hydrous conditions are weaker than those deformed under anhydrous conditions. The water fugacity for samples deformed under hydrous conditions at a confining pressure of 300 MPa and 1473 K is $\sim 300 \text{ MPa}$. Results are taken from R&D, Rybacki and Dresen (2000); C,H,&K, Chen et al. (2006); Mei and Kohlstedt (2000a); Chopra and Paterson (1984); and Bystricky and Mackwell (2001).

Table 2 Dependence of point defect concentrations on water fugacity, expressed as the exponent q in the relationship $[] \propto f_{\text{H}_2\text{O}}^q$, for several charge neutrality conditions for a transition-metal silicate

	$[Fe_{Me}']$ [h*]	$[Fe_{Si}']$	$[V_{Me}']$	$[(OH)_O]$ [p*]	$[H_{Me}']$	$[(2H)_{Me}^x]$	$[O']$	$[V_{Si}''']$	$[H_{Si}''']$	$[(2H)_{Si}^x]$	$[(3H)_{Si}^x]$	$[(4H)_{Si}^x]$
$[h^*] = 2[V_{Me}']$	0	0	0	1/2	1/2	1	0	0	1/2	1	3/2	2
$[p^*] = 2[V_{Me}']$	-1/6	1/6	1/3	1/3	2/3	1	1/3	2/3	1	4/3	5/3	2
$[p^*] = [Fe_{Si}']$	-1/4	1/4	1/2	1/4	3/4	1	1/2	1	5/4	3/2	7/4	2
$[h^*] = [H_{Me}']$	1/4	-1/4	-1/2	3/4	1/4	1	-1/2	-1	-1/4	1/2	5/4	2
$[p^*] = [H_{Me}']$	0	0	0	1/2	1/2	1	0	0	1/2	1	3/2	2

understanding and modeling mantle dynamics relies less on detailed models of creep processes and more on robust experimental results that can be extrapolated from laboratory to geologic conditions.

2.18.3.3 Role of Texture in Rock Deformation

Many deformed rocks exhibit textures defined by crystallographic alignment of the constituent mineral grains. This alignment arises from the viscous anisotropy inherent to most crystals, and strong crystallographic fabrics can therefore impart anisotropy in viscosity to an aggregate of grains. Texture development related to deformation is sensitive to deformation conditions, composition, and strain history. Several approaches have been formulated to simulate texture development and predict bulk constitutive behavior of rocks using constitutive equations derived from the deformation of single crystals. Thus, simulated textures and viscous anisotropy can be compared to those derived in the laboratory under known conditions and with known compositions to calibrate micro-mechanical models of rock deformation. In turn, those models can be used to interpret anisotropy in geophysical signals such as seismic velocity, electric conductivity, and lithospheric flexure.

2.18.3.3.1 Texture development during deformation

Single crystals deforming by the motion of dislocations change shape due to the operation of specific slip systems. For a force, F , applied to a crystal of cross-sectional area A , the shear stress resolved onto a slip system in the slip direction, σ_s , is defined by (Schmid and Boas, 1950, p. 105)

$$\sigma_s = \frac{F}{A} \cos \alpha \cos \beta \quad [64]$$

where α and β are the angles between the direction of the applied force and the Burgers vector and normal to the slip plane, respectively. The resolved shear stress results in a strain rate following the constitutive behavior outlined in Section 2.18.3.1.2. The term $\cos \alpha \cos \beta$ is often referred to as the Schmid factor. Individual slip systems can be characterized by a critical resolved shear stress, which is the resolved shear stress necessary for dislocations in that slip system to produce deformation at a given strain rate. The glide of dislocations yields a change in the shape of a single crystal, which is dominated by the strain resulting from the most favorable slip system, that is, the slip system with the most advantageous combination of low critical resolved shear stress and high Schmid factor. The

change in shape induces a rotation of the crystallographic reference frame relative to the direction of the applied force. Schmid and Boas (1950, pp. 58–63) demonstrated that this deformation is characterized (i) by the rotation of $\mathbf{b}$ toward the direction of an applied tensional force or (ii) by the rotation of the normal to the slip plane toward the direction of an applied compressional force. Because the rotation results in changes in the values of α and β , progressive deformation can lead to weakening or hardening of the crystal. In a polycrystalline rock, stresses and strain rates are partitioned among grains with a distribution of orientations. Although all grains are continually rotating, crystallographic textures can be developed if certain orientations are statistically favored (e.g., Wenk and Christie, 1991). For simple scenarios in which only a few slip systems are available, the orientation and shape of the crystallographic fabric can be used to infer the operative (dominant) slip planes and slip directions.

A wide range of experimental studies have linked texture development in rocks to deformation involving dislocations. As depicted in Figure 20, olivine-rich rocks deformed under dry, melt-free conditions in which $n > 1$ exhibit a crystallographic fabric with most [010] axes normal to the slip plane and most [100] axes parallel to the shear direction, consistent with intragranular deformation dominantly produced by (010)[100] slip (Bystricky et al., 2000; Carter and Avé Lallemant, 1970; Hansen et al., 2012b; Nicolas et al., 1973; Zhang and Karato, 1995; Zhang et al., 2000). This observation is anticipated based on experiments on single crystals, which demonstrate that (010)[100] is the weakest slip system under the relevant conditions (Bai et al., 1991; Durham and Goetze, 1977). The similarity between fabrics developed in the laboratory and those observed in naturally deformed rocks (e.g., Ismail and Mainprice, 1998) suggests that the same mechanisms are accommodating deformation in both cases (Figure 20). Notably, most of the available creep data for aggregates of olivine have been obtained on samples deformed in the dislocation-accommodated grain-boundary sliding regime. Thus, even when sliding along grain boundaries contributes significantly to deformation, intragranular deformation appears to control grain rotations and produce strong crystallographic fabrics.

Because the weakest slip system has a significant influence on the orientation of the resulting crystallographic fabric, transitions in the relative strengths of slip systems result in a change in the crystallographic fabric. The relative strengths of slip systems depend on chemical environment (Bai et al., 1991; Mackwell et al., 1985) and thermomechanical conditions (Raterron et al.,

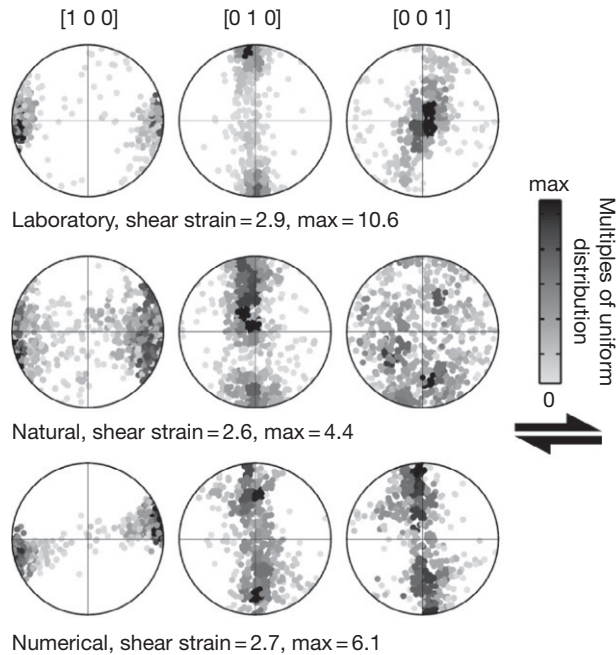


Figure 20 Olivine crystallographic fabrics observed in laboratory experiments, natural shear zones, and numerical simulations. All data are one point per grain plotted on equal-area lower hemisphere projections. Data from the laboratory are from a torsion experiment on an aggregate of Fo₅₀ (Hansen et al., 2014). Data from nature are from a shear zone in the Josephine peridotite (Warren et al., 2008). Data from numerical simulation are from a calculation using the viscoplastic self-consistent approach with code provided by Ricardo Lebensohn (Lebensohn and Tomé, 1993).

2007, 2009, 2012); therefore, crystallographic fabrics provide valuable indicators of the thermodynamic state during deformation. As an important example, Mackwell et al. (1985) demonstrated that for single crystals, (001)[100] slip becomes easier than (010)[100] slip with a small addition of water; subsequently, Jung and Karato (2001) observed the related fabric transition in olivine aggregates. Further details of transitions in crystallographic fabrics associated with changes in experimental conditions are described by Mainprice (2007) and Karato et al. (2008).

Several studies have formulated numerical descriptions of the development of crystallographic fabrics in rocks, as reviewed by Karato (2008, pp. 262–265) and Wenk and Christie (1991). Crystallographic fabric development in geologic materials is a complex mechanical problem because many minerals exhibit fewer than five independent slip systems such that the von Mises compatibility criterion is not satisfied (von Mises, 1928). Some of the most computationally efficient formulations describe bulk behavior and do not deal with the complexity of grain-grain interactions (Mühlhaus et al., 2004; e.g., Lev and Hager, 2008); unfortunately, the necessary assumptions limit their applicability. Models that track multiple grains are bounded by those that assume all grains are deforming either at the same stress (Reuss, 1929) or at the same strain rate (Bishop and Hill, 1951; Taylor, 1938) with more sophisticated approaches allowing both the stress and strain rate to vary between grains. Many approaches use a self-consistent formalism in which each grain

is considered to be interacting with a homogeneous surrounding medium (e.g., Lebensohn and Tomé, 1993). These methods include a second-order linearization (Castelnau et al., 2008; Ponte Castañeda, 2002) and an approximation to that linearization often referred to as the viscoplastic self-consistent model (Lebensohn and Tomé, 1993; Tommasi et al., 2000). Figure 20, which compares results from this latter approach to fabrics formed in naturally and experimentally deformed olivine-rich rocks, demonstrates that numerical simulations based on experimental results from deformation of single crystals can reasonably approximate deformation of aggregates, although significant differences remain.

2.18.3.3.2 Texture as a constraint on deformation mechanism

Because crystallographic fabrics are easily measurable and are, in general, directly related to the activity of dislocations during deformation, they are commonly used to infer the dominant deformation mechanism in both experimentally and naturally deformed rocks. As noted earlier in the text, strong crystallographic fabrics have been observed in laboratory experiments in which deformation involved dislocations. In contrast, relatively few experiments have been conducted in the diffusion creep regime to high enough strain to comment on fabric development. Samples from the few experiments that reached moderate strains in the diffusion creep regime exhibit either no or a relatively weak crystallographic fabric (Dell'Angelo and Olgaard, 1995; Fliervoet et al., 1999; Rutter and Brodie, 2004; Sundberg and Cooper, 2008). Thus, many studies have used the presence or lack of a crystallographic fabric to distinguish between deformation involving dislocations and that dominated by diffusion creep, respectively. However, several recent studies suggest that deformation by diffusion creep can result in relatively strong fabrics if there is significant anisotropy in grain shapes (Miyazaki, 2013; Wheeler, 2009) or anisotropy in diffusion or reaction kinetics (Sundberg and Cooper, 2008); thus, care must be taken if deformation mechanisms are inferred from crystallographic fabrics.

Several studies have used the strength of crystallographic fabrics measured in naturally deformed rocks to confirm extrapolations of laboratory-derived flow laws. Reductions in fabric strength have been correlated with the predicted transition from dislocation creep to diffusion creep or from dislocation-accommodated grain-boundary sliding to diffusion creep in plagioclase-rich mylonites (Mehl and Hirth, 2008), quartz-rich mylonites (Okudaira and Shigematsu, 2012), and olivine-rich mylonites (Linckens et al., 2011; Warren and Hirth, 2006). In these studies, the transition in deformation mechanism is hypothesized to result from reduced steady-state grain size of the primary phase due to dispersed secondary phases inhibiting grain growth (e.g., Olgaard, 1990). The relatively good agreement between transitions in crystallographic fabric strength and predicted transitions in deformation mechanism demonstrates the applicability of laboratory-derived constitutive equations to real-earth conditions.

2.18.3.3.3 Effect of texture on rock viscosity

In addition to being a valuable indicator of deformation mechanism, strong crystallographic fabrics result in macroscopically

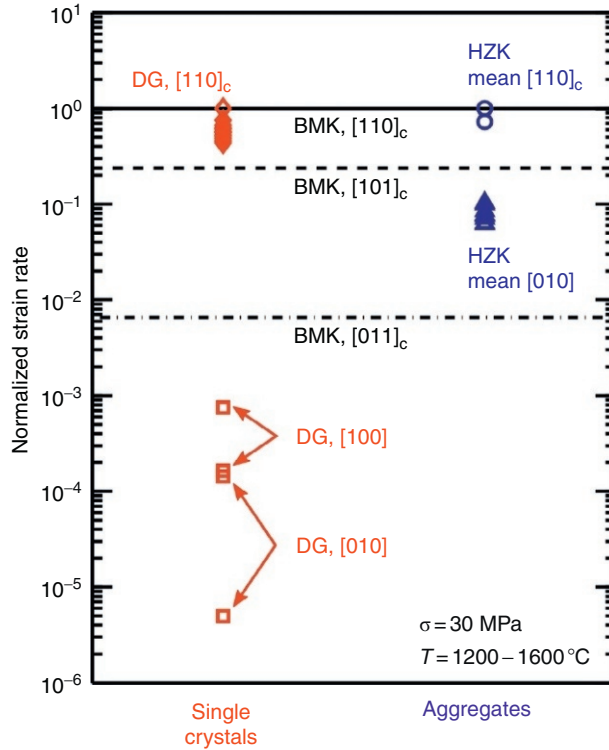


Figure 21 Normalized strain rates from experiments on both single crystals and polycrystalline aggregates illustrating the mechanical anisotropy of olivine. Single-crystal data are from Bai et al. (1991) (BMK) and Durham and Goetze (1977) (DG). Aggregate data are from Hansen et al. (2012a,b) (HZK). Strain rates are normalized by the highest rate in each group. Flow laws from Bai et al. (1991) are calculated for three different crystal orientations with the oxygen fugacity buffered by the Ni: NiO reaction with $T = 1200^\circ\text{C}$. Notation for crystal orientations follows Durham and Goetze (1977) and Bai et al. (1991). Because the strong crystallographic fabrics formed during the torsion experiments of Hansen et al. (2012a,b) have symmetry similar to olivine single crystals, data from torsion and tension experiments represent stress orientations similar to $[110]_c$ and $[010]$, respectively. Data from Durham and Goetze (1977) were collected at $T = 1600^\circ\text{C}$, and data from Hansen et al. (2012a,b) were collected at $T = 1200^\circ\text{C}$.

anisotropic mechanical behavior. Many minerals are mechanically anisotropic as evidenced by deformation experiments on single crystals of varying orientations. In Figure 21, results of deformation experiments on olivine single crystals reveal a variation of over two orders of magnitude in viscosity depending on which slip systems are activated (Bai et al., 1991; Durham and Goetze, 1977). Further, in experiments with applied compressive stresses along the primary crystallographic axes of olivine single crystals for which there is no resolved shear stress on the available slip systems, viscosity is over three orders of magnitude larger than for orientations with large Schmid factors (Durham and Goetze, 1977).

Many of the numerical simulations used to predict texture development in geologic materials have also been used to estimate the magnitude of viscous anisotropy in those materials. Such models are currently the primary source for estimating the magnitude and symmetry of viscous anisotropy in Earth (for a review, see Wenk, 1999). Geologic materials investigated in this

manner include ice (Castelnau et al., 1997; Lebensohn and Canova, 1996; Rudolph and Manga, 2012), halite (Siemes, 1974; Wenk et al., 1989a), calcite (Lebensohn et al., 1998; Tomé et al., 1991), quartz (Lister and Hobbs, 1980; Lister et al., 1978; Wenk et al., 1989b), olivine (Castelnau et al., 2008, 2009; Knoll et al., 2009; Lebensohn et al., 2010; Tommasi, 1998; Tommasi et al., 1999, 2000, 2009; Wenk and Tomé, 1999), and wadsleyite (Tommasi et al., 2004).

Several phenomenological constitutive models exist that describe the macroscopic behavior of anisotropic materials. In a manner similar to that used in elasticity theory, viscosity can be defined as a fourth-rank tensor, η_{ijkl} , which is related to the deviatoric stress tensor, σ_{ij} , and strain rate tensor, $\dot{\epsilon}_{kl}$, through the expression

$$\sigma_{ij} = 2\eta_{ijkl}\dot{\epsilon}_{kl} \quad [65]$$

where subscripts indicate tensor indices following the Einstein convention. Commonly, the viscosity tensor is assumed to have transverse isotropy, which reduces the total number of independent components to three (e.g., Han and Wahr, 1997). Simplifying the problem to two dimensions further reduces the viscosity tensor to two components (Christensen, 1987; Honda, 1986). Although this approach allows easy incorporation into geodynamic models, it suffers from being limited to Newtonian viscosity, that is, a constitutive equation with a stress exponent of $n = 1$.

A nonlinear form of a power-law flow law was first extended to multiaxial deformation by Odqvist (e.g., Odqvist et al., 1962). Written in terms of fluidity rather than viscosity, which is more useful for application to laboratory experiments, this power-law relationship is

$$\dot{\epsilon}_{ij} = \Phi_{ijkl}\sigma_{kl}\Pi_\sigma^{\left(\frac{n-1}{2}\right)} \quad [66]$$

where Φ_{ijkl} is the fluidity tensor (the inverse of the viscosity tensor), Π_σ is the second invariant of the deviatoric stress tensor, and n is the stress exponent. The von Mises equivalent stress is defined as $\sigma_e \equiv \sqrt{3\Pi_\sigma}$, which allows eqn [66] to be rewritten in Voigt notation as

$$\dot{\epsilon}_i = 3^{-\left(\frac{n-1}{2}\right)}\Phi_{ij}\sigma_j\sigma_e^{(n-1)} \quad [67]$$

Note that eqn [67] is equivalent to eqn [37] in Karato (2008). For the case in which the stress state is triaxial compression (i.e., $\sigma_1 > \sigma_2 = \sigma_3$ such that σ_e is equal to the differential stress) and the deformation maintains constant volume, the axial strain rate measured in the laboratory is given by

$$\dot{\epsilon}_1 = 3^{-\left(\frac{n-1}{2}\right)}\Phi_{11}\sigma_e^n \quad [68]$$

Note that, for triaxial compression, $\dot{\epsilon}_1 = \dot{\epsilon}_e$. If the stress state is simple shear (i.e., σ_6 is the only nonzero stress component), the shear strain rate measured in the laboratory is given by

$$\dot{\epsilon}_6 = \Phi_{66}\sigma_6^n \quad [69]$$

Note that, for simple shear, $\dot{\epsilon}_6$ and σ_6 are related to the equivalent strain rate, $\dot{\epsilon}_e$, and equivalent stress, σ_e , by $\dot{\epsilon}_e = 2\dot{\epsilon}_6/\sqrt{3}$ (where $2\dot{\epsilon}_6$ is the engineering shear strain rate) and $\sigma_e = \sigma_6\sqrt{3}$, respectively. If the material is isotropic, then $\Phi_{66} = 2(\Phi_{11} - \Phi_{12})$ and, through conservation of volume, $\Phi_{66} = 3\Phi_{11}$

and $\Phi_{12} = -\frac{1}{2}\Phi_{11}$. Thus, the magnitude of viscous anisotropy can be assessed through comparison of the components of the fluidity tensor. A useful example is

$$\delta = \frac{\Phi_{66}}{3\Phi_{11}} \quad [70]$$

For an isotropic material, $\delta = 1$. If eqns [68] and [69] are combined with eqn [70], then

$$\delta = \left(\frac{\dot{\epsilon}_{e,s}}{\dot{\epsilon}_{e,n}} \right) \left(\frac{\sigma_{e,n}}{\sigma_{e,s}} \right)^n \quad [71]$$

where the subscripts s and n denote equivalent values measured in simple shear and triaxial compression or tension, respectively. Note that if the value of δ is assessed at constant equivalent stress, then eqn [71] reduces to the form used by Hansen et al. (2012a,b).

Relatively few laboratory-based experiments have measured the magnitude of viscous anisotropy in rocks. Muto et al. (2011) deformed quartz single crystals in three different orientations to high enough strains that dynamic recrystallization produced fine-grained aggregates with crystallographic fabrics with orientations controlled by the orientation of the starting single crystal. Their experiments demonstrate that slip on the basal plane is up to an order of magnitude less viscous than slip on the prism plane. Wendt et al. (1998) conducted experiments on cores of natural dunite with a preexisting crystallographic fabric. Although these experiments experienced extensive brittle and semibrittle deformation behavior, the viscosity was qualitatively determined to be a function of the orientation of the applied stress relative to the orientation of the preexisting fabric. As depicted in Figure 20, Hansen et al. (2012a) performed torsion tests on olivine aggregates and demonstrated that strong crystallographic fabrics favor slip on the weakest slip system and reduce the bulk flow stress by $\sim 30\%$ relative to an isotropic aggregate. Subsequent tension tests were performed on samples previously deformed in torsion with the tensional stress applied along the dominant [010] axis orientation, a geometry that minimizes the resolved shear stress on the available slip systems (Hansen et al., 2012a). These latter tests demonstrated that the viscosity of textured olivine aggregates can vary by over an order of magnitude depending on the orientation of the applied stress relative to the crystallographic fabric. However, the maximum anisotropy observed is still multiple orders of magnitude smaller than the anisotropy measured on olivine single crystals, which suggests that small misorientations between grains and the average orientation significantly affect the macroscopic viscosity.

Several lines of field evidence indicate that viscous anisotropy plays an important role in lithospheric deformation. The examination of mantle shear zones exposed in orogenic peridotites demonstrates that crystallographic fabrics have a controlling influence on shear zone orientation (Michibayashi and Mainprice, 2004). Further, the magnitude of localization in these shear zones can only be accounted for if viscous anisotropy is taken into account (Skemer et al., 2014). Investigations of upper mantle seismic anisotropy in regions of incipient rifting observe strong correlations between the orientation of seismic anisotropy and the trend of the rift axes (Vauchez et al.,

1998). Additionally, some studies of lithospheric flexure have noted that the flexural rigidity of the lithosphere is anisotropic and the orientation of that anisotropy correlates well with the orientation of seismic anisotropy (Audet and Mareschal, 2004; Kirby and Swain, 2006; Simons and Van der Hilst, 2003).

2.18.4 Upper Mantle Viscosity

In this section, viscosity profiles for the oceanic upper mantle are calculated. Radial gradients in upper mantle viscosity are responsible for some of the key geodynamic characteristics of terrestrial planets. For instance, lithospheric plates act as a mechanical boundary layer to the convecting mantle because of a sharp transition to significantly lower viscosities in the underlying asthenosphere. Additionally, the presence of a sublithospheric minimum in viscosity (i.e., the asthenosphere) may be crucial for the operation of plate tectonics (Höink et al., 2012). Three sets of conditions are considered here: First, to examine the first-order effects of temperature and pressure, viscosity profiles are calculated assuming dry, melt-free conditions. Second, viscosity is calculated assuming the shallowest portions of the mantle are dry and the deeper portions have a water content of 800 ppm H/Si. Third, viscosity is calculated assuming the shallowest portions of the mantle are melt-free and the deeper portions are partially molten with a total melt fraction of 0.01.

Laboratory results for dunite (i.e., olivine volume fraction $>95\%$) – rather than for harzburgite or lherzolite – are used because it is the only rock for which data are available over a wide range of upper mantle conditions. Justification for this choice is based on the observations that olivine is the major mineral in the upper mantle and that, under conditions for which data are available, the flow behavior of dunite is nearly identical to that of lherzolite (Zimmerman and Kohlstedt, 2004). Calculations are carried out assuming that dislocation creep, dislocation-accommodated grain-boundary sliding, and diffusion creep are all contributing to the strain rate independently. Flow-law parameters for dislocation creep and diffusion creep in olivine aggregates are largely taken from Hirth and Kohlstedt (2003) with the activation volume for wet dislocation creep taken to be $20 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ (Mei and Kohlstedt, 2000b), a value consistent with recent experiments on single crystals (Girard et al., 2013). Flow-law parameters for dislocation-accommodated grain-boundary sliding and a modification of the preexponential constant in the diffusion creep flow law are taken from Hansen et al. (2011). Grain size is assumed to be at the steady-state value described by the grain size–stress relationship determined experimentally by Karato et al. (1980). Activation volumes for dry dislocation creep and dislocation-accommodated grain-boundary sliding flow laws are taken from the results of experiments conducted on single crystals of olivine (Raterron et al., 2009, 2012). Because dislocation creep requires activation of all three primary dislocation slip systems in olivine to satisfy the von Mises criterion (von Mises, 1928), we suggest that the activation volume for dislocation creep is that of a single crystal deforming by the motion of dislocations of the strongest slip system, (010) [001] ($3 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$). Similarly, because dislocation-accommodated grain-boundary sliding appears to require only the activation of a single slip system (Goldsby and Kohlstedt,

2001; Hirth and Kohlstedt, 2003), we suggest that the activation volume for grain-boundary sliding is that of a single crystal deforming by the motion of dislocations of the weakest slip system (010)[100] ($12 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$). Because (010)[001] slip is predicted to become easier than (010)[100] slip at depths greater than $\sim 240 \text{ km}$ (Raterron et al., 2012), we implement a corresponding switch in activation volume. Most calculations were carried out assuming that the differential stress is constant throughout the upper mantle. Values of the differential stress were chosen to yield magnitudes of viscosity that result in plate velocities of approximately 5 cm year^{-1} assuming a Couette flow geometry, which is equivalent to an average strain rate of $4 \times 10^{-15} \text{ s}^{-1}$ for a 400 km thick upper mantle.

2.18.4.1 Effect of Temperature and Pressure

In Figure 22(a), viscosity is depicted as a function of depth for dry, melt-free olivine. The temperature as a function of depth was determined for 50 million-year-old lithosphere using a

half-space cooling model and an adiabatic geotherm with a potential temperature, T_p , of 1350°C (Turcotte and Schubert, 2002, pp. 185–187). The resulting temperature profile is illustrated in Figure 22(b). A differential stress of $\sigma = 0.8 \text{ MPa}$ was required to produce the desired plate velocity. A second calculation is depicted in which the rate of viscous energy dissipation per unit volume, $\sigma\dot{\epsilon}$, is assumed to be constant (e.g., Christensen, 1989). For this second calculation, a dissipation rate of $\sigma\dot{\epsilon} = 4 \times 10^{-9} \text{ Pa s}^{-1}$ was required to produce the desired plate velocity.

Because of the significant temperature dependence of the viscosity of mantle rocks, the shallowest and thus coldest portions of the upper mantle are characterized by large viscosities. Therefore, the thermal boundary layer inherent to the half-space cooling model yields a distinct mechanical boundary layer characterized by a viscosity that decreases by approximately a factor of 10 per 10 km.

The calculated viscosity profiles are also characterized by a minimum in viscosity at $\sim 150 \text{ km}$, due to the increasing effect of pressure relative to that of temperature. Minimum viscosities

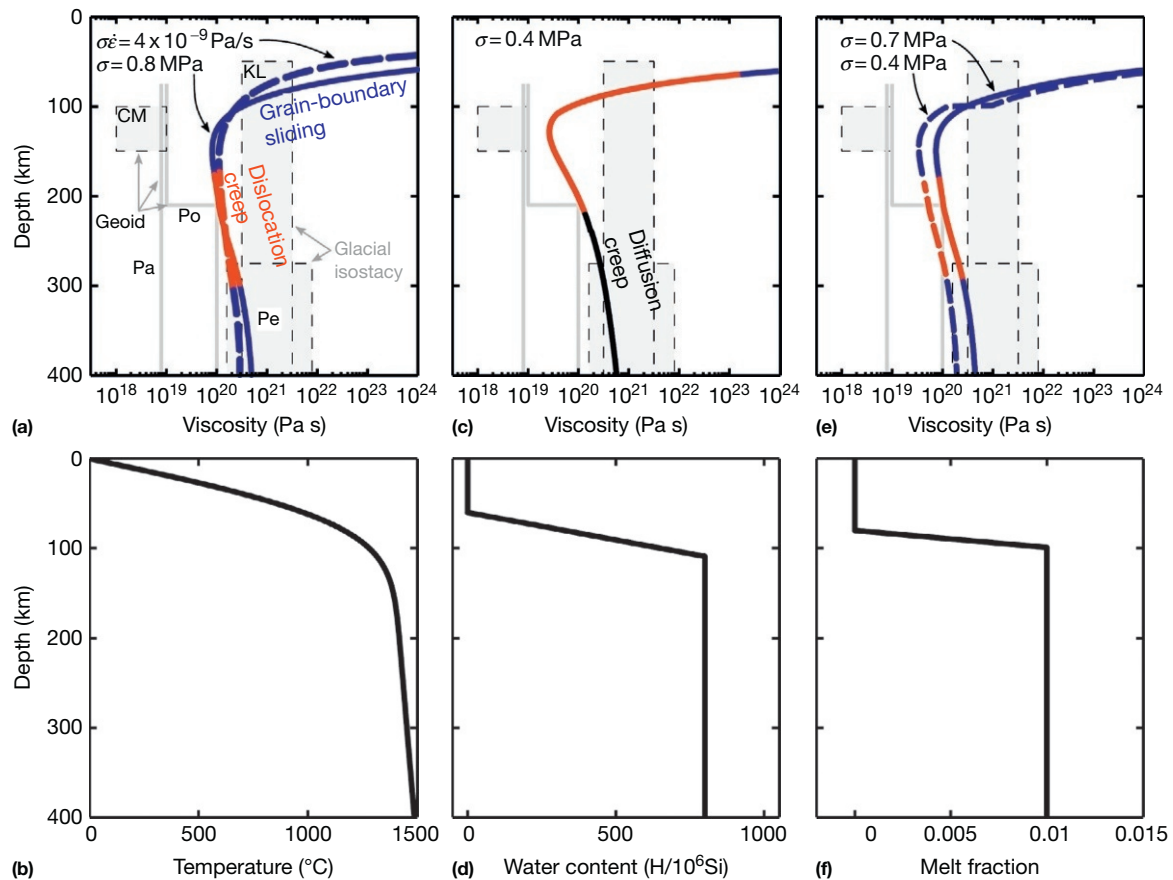


Figure 22 Viscosities as a function of depth in the upper mantle calculated using laboratory-derived flow laws for dunite. (a) Viscosities for dry, melt-free conditions calculated using both uniform stress (solid line) and uniform viscous dissipation rate (dashed line) and the temperature profile for 50 million-year-old lithosphere depicted in (b). The temperature profile in (b) was used for all calculations. Viscosity profiles are colored according to the mechanism of deformation that contributes most to the strain rate (dislocation creep = red; grain-boundary sliding = blue; diffusion creep = black). Viscosity profiles are compared to estimates from geophysical observations denoted by gray boxes and lines. Citation abbreviations are as follows: CM, Craig and McKenzie (1986); KL, Kaufmann and Lambeck (2002); Pa, Panet et al. (2010); Pe, Peltier (1998); Po, Pollitz et al. (2006). (c) Viscosities for hydrated conditions calculated using the profile of water content depicted in (d). (e) Viscosities for partially molten conditions calculated using the profile of melt fraction depicted in (f). Calculations for partially molten conditions were conducted assuming either homogeneously distributed melt (solid line) or melt segregated into melt-rich bands (dashed line).

are 8.1×10^{19} and 1.1×10^{20} Pa s for calculations assuming constant stress and constant dissipation rate, respectively. Below the viscosity minimum, viscosity increases by a factor of ~ 1.01 per 10 km. We note that the viscosity gradient below the viscosity minimum is distinctly less pronounced than previous calculations of mantle viscosity using laboratory-derived flow laws (e.g., [Hirth and Kohlstedt, 2003](#)) because of the recently determined activation volumes used here. Thus, solely the effects of temperature and pressure result in both a low-viscosity zone and a mechanical boundary between the lithosphere and asthenosphere.

Several interesting observations can be made regarding the relative contributions of different mechanisms to deformation. First, diffusion creep never dominates except in the coldest portions of the lithosphere. Instead, dislocation-accommodated grain-boundary sliding governs over the largest volume of the upper mantle. With increasing depth, the dominant mechanism switches to dislocation creep at ~ 175 km due to the different activation volumes for the hardest and easiest slip systems. Interestingly, the primary deformation mechanism again becomes dislocation-accommodated grain-boundary sliding at ~ 300 km because of the change in relative slip system strength. The observed distribution of deformation mechanisms is at odds with previous studies that have suggested diffusion creep is the dominant mechanism in the deeper portions of the upper mantle based on the lack of seismic anisotropy at those depths (e.g., [Karato and Wu, 1993](#)). We point out, however, that the magnitude of seismic anisotropy is a strong function of the total strain (e.g., [Bystricky et al., 2000](#); [Hansen et al., 2014](#)). Since the strain can be multiple orders of magnitude larger near the viscosity minimum than at the base of the upper mantle, there can be significant gradients in the magnitude of seismic anisotropy even if dislocation creep or dislocation-accommodated grain-boundary sliding is the dominant flow mechanism (e.g., [Behn et al., 2009](#); [Podolefsky et al., 2004](#)).

2.18.4.2 Effect of Water

In [Figure 22\(c\)](#), viscosity is plotted as a function of depth for conditions similar to those used in the previous section but with the addition of a hydrated sublithospheric mantle. We construct a profile of water content as a function of depth following the argument of [Hirth and Kohlstedt \(1996\)](#). The uppermost portion of the mantle is considered to be free of water-related defects due to the extraction of water from mantle peridotites during partial melting at a mid-ocean ridge axis. We assume that olivine in the lower portion of the upper mantle has a constant water content of 800 ppm H/Si and that the water content gradually transitions from 0 to 800 ppm H/Si between 60 and 110 km depth. The increase in water content is formulated as a linear function of depth, which is expected for batch melting ([Hirth and Kohlstedt, 1996](#)). We note that using a nonlinear increase in water content, as expected for fractional melting, does not significantly affect the results of this calculation. The water content as a function of depth is depicted in [Figure 22\(d\)](#).

The resulting viscosity profile is very similar to that depicted in [Figure 22\(a\)](#). Gradients in viscosity at shallower depths than the viscosity minimum are comparable to those for the dry case.

However, the magnitude of the viscosity minimum (2.8×10^{19} Pa s) is significantly less than for the dry case and the viscosity gradient below the viscosity minimum (factor of 1.6 per 10 km) is greater than for the dry case. Weakening associated with water-related defects is manifested in the differential stress being a factor of 2 lower than that for the dry case.

The dominant deformation mechanisms are distinctly different in the hydrated case compared to the dry case, primarily due to the absence of dislocation-accommodated grain-boundary sliding under hydrous conditions. This mechanism dominates in the dry upper 60 km of the model, but the dominant mechanism becomes dislocation creep once the water content increases at depths greater than 60 km. Diffusion creep becomes the dominant mechanism at a depth of 220 km and remains the dominant mechanism throughout the remainder of the upper mantle.

2.18.4.3 Effect of Melt and Melt Segregation

[Figure 22\(e\)](#) depicts the viscosity of the upper mantle calculated assuming dry conditions, as in [Figure 22\(a\)](#), but including a small volume of melt. The melt fraction is assumed to be $\phi = 0$ in the upper 80 km and to increase linearly to $\phi = 0.01$ by 100 km depth ([Langmuir et al., 1992](#)).

The effect of a partial melting on viscosity is calculated using eqn [56] with $\alpha = 35$ for both dislocation creep and dislocation-accommodated grain-boundary sliding flow laws and $\alpha = 30$ for the diffusion creep flow law. Based on experiments on partially molten aggregates of olivine + chromite + MORB ([Holtzman et al., 2003a,b](#); [King et al., 2010](#)), [Holtzman et al. \(2012\)](#) demonstrated that partially molten systems in which the melt segregates into melt-rich bands can have dramatically reduced viscosities. [Figure 22\(e\)](#) presents a second calculation that takes the effect of stress-driven melt segregation into account. Based on [Holtzman et al. \(2012\)](#), the total strain rate is taken to be

$$\dot{\epsilon} = a_b \dot{\epsilon}_b + \dot{\epsilon}_n a_n \quad [72]$$

where the subscripts b and n denote band (melt-enriched) and nonband (melt-depleted) regions, respectively, and a is the volume fraction of those regions. The volume fractions are given by

$$a_b = \frac{\phi_t S}{\phi_b} \quad [73a]$$

$$a_n = 1 - a_b \quad [73b]$$

where ϕ_t and ϕ_b are the total melt fraction and the melt fraction in the bands, respectively. The total melt fraction is set to $\phi_t = 0.01$, and the melt fraction in the bands is set to $\phi_b = 0.15$. S describes the degree of melt segregation, which varies from 0 to 1 for a homogeneously distributed melt and a completely segregated melt, respectively. We use a value of $S = 0.7$, which [Holtzman et al. \(2012\)](#) determined to be the steady-state value.

Both calculations involving melt-rich conditions result in viscosity profiles similar to the dry, melt-free case depicted in [Figure 22\(a\)](#). Viscosity gradients above and below the viscosity minimum closely match those in [Figure 22\(a\)](#). Additionally,

the dominant deformation mechanisms and their depth ranges are approximately the same as in the dry, melt-free case. The melt-rich case without segregation results in a viscosity minimum (7.5×10^{-19} Pa s) similar in magnitude to the melt-free case, but the stress, $\sigma = 0.7$ MPa, is slightly less than the melt-free case. Notably, the melt-rich case with segregation results in a factor of eight reduction in viscosity at 100 km depth, corresponding to the increase in melt fraction. This sharp viscosity gradient illustrates the important role of stress-driven melt segregation in local viscosity reduction and the localization of deformation. The observed viscosity drop results in smaller minima in viscosity (3.4×10^{-19} Pa s) and stress (0.4 MPa) than in the case without segregation.

2.18.4.4 Comparison to Geophysical Observations

Several geophysical observations place constraints on the viscosity structure of the upper mantle. In [Figure 22\(a\)](#), [22\(c\)](#), and [22\(e\)](#), calculated viscosity profiles are compared to estimates of upper mantle viscosity from observations of glacial isostatic adjustment and analyses of the geoid. Estimates of the globally averaged upper mantle viscosity from isostatic adjustment during the retreat of late Pleistocene ice sheets, as are illustrated in [Figure 22](#), range from approximately 10^{20} to 10^{22} Pa s ([Kaufmann and Lambeck, 2002](#); [Peltier, 1998](#)). Estimates of upper mantle viscosity from analyses of the geoid, as illustrated in [Figure 22](#), are based either on geoid observations near oceanic fracture zones ([Craig and McKenzie, 1986](#)) or on post-seismic variation in the geoid after the 2004 Sumatra-Andaman earthquake ([Panet et al., 2010](#); [Pollitz et al., 2006](#)). Estimates of viscosity based on post-seismic deformation range from 10^{18} to 10^{19} Pa s in the 100–150 km depth range and from 10^{19} to 10^{20} Pa s in the deep upper mantle.

The calculations based on laboratory-derived flow laws depicted in [Figure 22](#) correlate well with certain aspects of the geophysical observations and poorly with others. The viscosities predicted between depths of 100 and 400 km fall into a relatively narrow window ($10^{19.5}$ to $10^{20.5}$ Pa s). The predicted values near the base of the upper mantle overlap with those predicted by investigations of glacial isostatic adjustment. However, predicted viscosities are at least a half an order magnitude larger than estimates from observations of the geoid. Notably, none of the three sets of calculations (dry, wet, melt-rich) predict geophysically observed viscosity profiles significantly better than any of the others.

There are several potential explanations for the discrepancies between viscosities determined by geoid observations and those predicted by constitutive models. First, the age of the lithosphere in the region of the Mendocino Fracture Zone, for which the geoid was modeled ([Craig and McKenzie, 1986](#)), is significantly younger than that used to predict the thermal structure of the upper mantle in our calculations. Second, the viscous portion of the deformation subsequent to the 2004 Sumatra-Andaman earthquake was geologically fast and therefore characterized by small strains, a situation more akin to the transient portion of a stress-change test in the laboratory ([Freed et al., 2012](#)). For small strains after a stress increase, the viscous deformation of crystalline materials is typically characterized by a gradual increase in viscosity until a steady state is reached (e.g., [Takeuchi and Argon, 1976](#)). The flow laws used in our

calculations are for steady-state deformation, which thus overestimate the viscosity for small strain deformation. Third, both stresses and strain rates during post-seismic deformation are likely increased relative to background tectonic values. Because the viscous deformation of the uppermost mantle is almost certainly non-Newtonian (i.e., stress exponent $n > 1$), an increase in stress results in a decrease in viscosity. Fourth, because our calculation is constrained to a set average strain rate, only a larger gradient in the viscosity as a function of depth allows for a lower viscosity minimum. Because the total accumulated strain in the upper mantle likely varies over multiple orders of magnitude as a function of depth (e.g., [Behn et al., 2009](#)), incorporating strain into constitutive models (e.g., [Hansen et al., 2012a,b](#)) would potentially result in large enough viscosity gradients to match predictions from geoid observations. With these caveats in mind, we suggest that particular attention must be made to thermal structure, time-scale of deformation, stress during deformation, and deformation history in comparing different estimates of viscosity.

2.18.5 Concluding Remarks

While the good agreement between laboratory and field observations for the viscosity structure of the upper mantle is encouraging, even exciting, several important areas remain that require experimental investigation of the rheological properties of mantle rocks. Possibly the most obvious void is the paucity of deformation studies on transition zone and lower mantle minerals and rocks. Progress in this field has been slow, largely due to a lack of apparatuses capable of carrying out experiments under well-controlled thermomechanical conditions at very high pressures. However, recent developments combining a new generation of deformation apparatuses such as the deformation-DIA (D-DIA) and the rotational Drickamer apparatus (RDA) with high-intensity, synchrotron-produced x-rays hold promise for significant progress in this area (e.g., [Durham et al., 2009](#); [Hustoft et al., 2013](#); [Mei et al., 2010](#); [Raterron et al., 2011, 2012](#); [Xu et al., 2005](#)).

For the upper mantle, further work is needed to quantify the deformation behavior in the low-temperature plasticity regime, particularly under hydrous conditions, for application to studies of deformation of the lithosphere. Furthermore, laboratory (e.g., [Jung and Karato, 2001](#)) and seismic (e.g., [Mainprice et al., 2005](#)) observations indicate that a transition in slip system occurs below a depth of ~ 250 km in Earth's upper mantle, related to changes in water, stress, and/or pressure conditions. At present, flow laws for the upper mantle are primarily based on experiments carried out at relatively modest pressures for which measurements of lattice-preferred orientations indicate that deformation in olivine is dominated by dislocations with [100] Burgers vectors. If dislocations with [001] Burgers vectors become important in deeper portions of the upper mantle, the flow law determined at very high pressures may deviate from that extrapolated from lower-pressure conditions ([Cordier et al., 2012](#); [Couvry et al., 2004](#); [Mainprice et al., 2005](#); [Raterron et al., 2011, 2012](#)).

Finally, to date, most studies of plastic deformation of rocks have concentrated on steady-state creep with little attention given to transient deformation. While a steady-state approach

may describe convective flow in the mantle reasonably well, it cannot provide an adequate description of deformation that occurs in an environment for which thermomechanical conditions are changing and microstructures are simultaneously evolving (e.g., Evans, 2005). This point has been appreciated by a number of researchers, some of whom have taken a state-variable or mechanical equation-of-state approach (e.g., Covey-Crump, 1994, 1998; Lerner and Kohlstedt, 1981; Rutter, 1999; Stone et al., 2004). Such approaches will be critical in the development of the next generation of constitutive equations that must be capable of describing flow in regions such as shear zones and metamorphic belts in which changes in thermal and chemical environment – including composition of fluids and evolution of material's parameters (e.g., dislocation density, grain size, and lattice-preferred orientation) – occur continuously.

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2.19 Properties of Rocks and Minerals – Diffusion, Viscosity, and Flow of Melts

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2.19.1 Mass and Momentum Transport in Melts: Georelevance

2.19.1.1 Role of Melts in Earth Differentiation

The differentiation of the Earth is generally thought to have been accomplished in the presence of the molten phase (Wood et al., 2006). This picture extends from the scale of global differentiation into core, mantle, and crust to the differentiation into upper and lower sections of each and down to the scale of local differentiation providing chemical specialization of great extremes within the crust, the latter with their global significant economic importance. Nothing is more central to this picture than the transport properties of magma. With lower viscosities and possessing higher diffusivities than their neighboring solid phases, the melts involved in these processes are the material conduit for chemical transport from one reservoir to another. One needs but to pose the question of differentiation efficiency on a cool sub-solidus body to appreciate the meaning of this attribute of the terrestrial planets.

2.19.1.2 Melt-Bearing Reaction Kinetics

Equally significant in the relevance of melt transport properties to Earth processes is the observations that have been made regarding the relationship between melt viscosity and the diffusivities of melt components (Dingwell, 1990; Hofmann, 1980; Mungall, 2002; Mungall et al., 1999; Shimizu and Kushiro, 1984). The kinetics of reactions within the Earth's interior may be substantially controlled by the diffusivities of chemical components present in the reacting system. In general, diffusivities in the molten state are higher than in the solid state equivalent phases. Reactions in the presence of a melt phase may thus be strongly influenced by the diffusivities of components in the melt phase itself. For this reason, the experimental investigation and the systemization of results of chemical and trace diffusivities in silicate melts have been intensively pursued in the past decades. Systematization of the results in terms of the relationship to viscosity has revealed some interesting and useful approximations, which are discussed in detail in the succeeding text.

2.19.1.3 Magma Transport at Depth

The transport of magmas at depth is essentially controlled by the presence of stress gradients, vertical or otherwise. As such, the rheology of the magma is the coefficient of material response that scales the deformation of the magma body and its transport relative to neighboring rock masses. Experimental recognition of the wide range of magnitude of rheology of magma, together with its variable dependence on temperature, chemical composition, physical state, pressure, and (variably) strain rate, has generated a rich literature on the deformation of magma in the deep Earth. Central to all of these considerations has been the premise that during magma deformation and transport, conditions obtain, which permit the plastic deformational response of the magma. Under such circumstances, the rheological literatures of liquid silicates, of crystal and/or bubble suspensions, and of partially molten rock, all play major roles in filling out our physical picture of magma rheology at depth (Dingwell et al., 1993).

2.19.1.4 Magma Mixing, Mingling, and Unmixing

Multicomponent silicate melts are stable over very wide ranges of temperature, pressure, and composition. Further, within the Earth's mantle and crust, there is ample evidence, both textural, chemical and by geophysical inference, for the temporal coexistence and juxtaposition/interference of distinct melt batches within regional magmatic terrains. Thus, the phenomena of magma mingling (physical mixing) and mixing (chemical mixing) are now thought to be common in magmatic systems, often serving to precondition subvolcanic systems for subsequent eruptions. Magma mingling mixing occurs between magmas that are, often via extensive differentiation, very different in composition (e.g., basalt–rhyolite). Magma mingling and mixing also occurs between chemically distinct but quite similar compositions in subvolcanic environments. Evidence of both is provided most dramatically in coerupted mingling lava products. The kinetics of magma mingling and mixing are controlled by the relative viscosities and the chemical diffusivities of the melts, respectively. Here, the question of turbulence in magma mingling remains largely uninvestigated.

2.19.1.5 Volcanic Ascent and Eruption

There is hardly a more spectacular demonstration of the influence of the transport properties on melt transport than the eruption of a volcano. The range of eruptive styles of volcanic eruptions, from highly explosive Plinian eruptions, through the slow creep of rheomorphic flows, to the ready flow of rivers of lava over tens of kilometers, is determined by a series of conditions that are either directly or indirectly linked to the viscosity of the melt (Dingwell, 1996, 1998a,d). The rapidity of volcanic ascent and eruption leads to a number of consequences for the flow of magma. The dominant role of solid–liquid reactions in determining the differentiation of liquids and their transport at depth gives way to the relatively rapid generation of thermal and rheological consequences of effects such as the exsolution of volatile phases (Bagdassarov and Dingwell, 1992, 1993a,b), the strain rate-driven onset of shear thinning (Dingwell and Webb, 1989a,b, 1990; Webb

and Dingwell, 1990a,b), and even the development of viscous dissipation (Costa and Macedonio, 2003; Rosi et al., 2004; Vedeneeva et al., 2005). Numerical simulations, of increasingly critical importance in testing the consequences of mechanistic hypotheses for transport during eruptions, are critically dependent on an adequate characterization of melt viscosity (Dingwell, 1998d; Papale, 1999).

2.19.1.6 Emplacement of Natural Glass

Viscosity also serves to quantify the conditions for the transformation from the liquid to the glassy state volcanism, at least on the Earth and Moon, commonly generates volcanic glass. The observation of abundant survival of this unstable thermodynamic and fluid dynamic state is a tribute to the sluggishness of crystal nucleation and growth kinetics in silicates, combined with the rapid cooling history provided in volcanic settings. The disequilibrium nature of the glassy state means that the properties of the glass phase are path-dependent (Moynihan et al., 1974, 1976a,b; Tool, 1946; Tool and Eichlin, 1931). This, in turn, leads to the conclusion that the glass properties can be used to obtain information on the conditions of their emplacement (Giordano et al., 2005; Gottsmann et al., 2002; Stevenson et al., 1995). This possibility has been exploited in recent years using calorimetric techniques to determine the effective viscosity at the glass transition and thus constrain the cooling history of natural glass (Gottsmann and Dingwell, 2001a,b, 2002; Gottsmann et al., 2004; Wilding et al., 1995, 1996a,b, 2000). The striking conclusion is that hyaline volcanic facies can endure a very wide range of effective cooling histories and can suffer several transects from liquid to glassy behavior during their emplacement.

2.19.2 Dynamics and Relaxation in Melts

2.19.2.1 A Note on the Definition of Terms

This chapter is entitled 'Properties of Rocks and Minerals – Diffusion, Viscosity, and Flow of Melts.' With that, it is important to note here that the term 'melt' is commonly very loosely defined. The term implies perhaps 'something which was created by melting.' This definition alone, however, says nothing to the fundamental nature of the properties of the system. Yet, it is the liquid-like values of the transport properties of the 'melt' phases that lend it its greatest significance with respect to the Earth sciences. Here, we will follow the usage that the melt phase describes an amorphous, typically silicate, phase whose properties may be either liquid-like or solid-like, depending on the environment and the conditions of the natural transport process, the experiment or the simulation in which the melt exists. In this sense, the phenomenology of the melt's response will define its behavior as a liquid or as a solid, or, in the terms to be employed here, as a liquid or a glass (Dingwell and Webb, 1990).

2.19.2.2 Structural Relaxation

The nature and phenomenology of structural relaxation in silicate melts, well-appreciated in the glass and ceramic literature as well as in modern chemistry (e.g., Angell et al., 2000),

has also been described in the context of mineral physics, petrology, and volcanology in a way that brings its relevance to the Earth sciences to the fore (Dingwell, 1995a,b; Dingwell and Webb, 1989a,b). The fundamental picture of liquid structure upon which the atomistic interpretation of its relaxation ultimately rests has been intensively investigated using a wide range of spectroscopic techniques. It is not the task of this chapter to review those structural studies for which ample summaries already exist (Mysen, 1988; Mysen and Richet, 2005; Stebbins et al., 1995). Rather, it should be noted here that almost all of the fundamental systematics and phenomenology of structural relaxation have been mapped out prior to the modern spectroscopic analysis of melt structure. This was made possible by using physical properties of the melt phase as proxies for its structural state. Arguably, the first attempt to do so is provided by the definition of a state parameter of glass, the so-called fictive temperature commonly attributed to Tool (1946). The variation of the structure of the melt was obtained via the measurement of a precisely determined physical property of the glassy state (density and refractive index) in the quenched state, as well as during the thermal recycling (heat capacity) (e.g., Narayanaswamy, 1971, 1988). A graphic illustration of the variation of fictive temperature with heating and cooling through the glass transition is provided in Figure 1.

2.19.2.3 Spectroscopic Observation of Structural Relaxation

Spectroscopic investigations of silicate melts have been highly successful in the elucidation of various aspects of the coordination of individual cations and anions in the silicate melt structure as well as information on the degree of connectivity of tetrahedral structural units (Q species) in silicate melts (Mysen and Richet, 2005; Stebbins et al., 1995). The success of such studies raises the question of whether structural relaxation can be investigated directly by using spectroscopic species data. There are several possible experimental protocols

(Dingwell, 1995a). Firstly, the structure of carefully quenched silicate glasses can be treated via fictive temperature analysis in order to obtain the temperature dependence of species concentration involved in homogeneous equilibria (Dingwell and Webb, 1990; Liu et al., 1987, 1988). Secondly, high-temperature, high-pressure spectroscopic investigations may directly record the temperature dependence of speciation and contain thereby the observation of the inflection in temperature dependence of speciation marking the glass transition temperature (Nowak and Behrens, 1995; Shen and Keppler, 1995). Thirdly, the high-temperature equilibration of species may be monitored in the so-called time series relaxation experiments where the quenched products are analyzed for the approach to equilibrium recorded by spectroscopic analysis of their species concentrations (Zhang et al., 1995, 1997). Fourthly, the spectroscopic investigation of silicate melts at high temperatures has resulted in a series of estimates of the timescales for relaxation through self-diffusion of the fundamental structural units being spectroscopically resolved. Nuclear magnetic resonance studies of the mobility of network-forming components in silicate melts have linked the relaxation of Si–O bonds between structural units contain variable numbers of nonbridging oxygens closely to the timescale of viscous flow (Stebbins, 1995). This close link between the relaxation of structural units as small as individual bridging bonds and the macroscopic relaxation of shear stress is strong evidence for the exclusion of large flow units involving some sort of polyanionic units (polymers) during the flow of silicate melts. In fact, there is no clear evidence for a polymeric nature of the structure of silicate melts based on physical properties. Nevertheless, polymer-based models for the activity and solubility of chemical components appear to be capable of predicting the chemical properties of melts (Moretti, 2005).

2.19.2.4 Phenomenology of the Glass Transition

The phenomenology of the glass transition is an ancient observation associated with glassmaking in prehistoric times. The fundamental observation is the transformation of the properties of a melt from those of a liquid to those of a solid, or vice versa. For certain properties, the transformation is qualitative in nature, for example, the development of rigidity in the glassy state. For most properties however, the transition is somewhat more subtle, yet quantitative determination of the effect of the glass transition on temperature-dependent properties such as density, compressibility, electrical conductivity, and heat capacity are a major source of quantitative information on the properties of silicate melts in general. The fundamental phenomenology of the glass transition can be illustrated with the example of the temperature- and state-dependent properties, thermal expansivity and heat capacity (Figure 2).

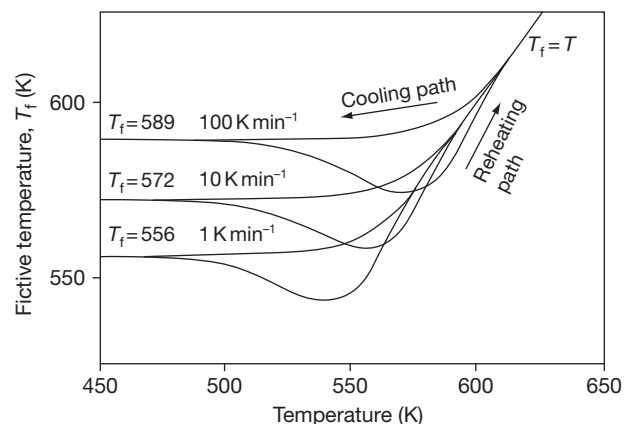


Figure 1 The variation of fictive temperature with temperature during the cooling of a supercooled liquid into the glassy state and during the heating of a glass into the supercooled liquid state. The fictive temperature is a proxy for all structure-dependent properties of the melt. Fictive temperature equals temperature in the liquid state, is constant in the glassy state, and exhibits a hysteresis in the glass transition region that depends on heating/cooling rate and the temperature dependence of viscosity and structure.

2.19.2.5 Atomistic Origin of Relaxation

The advent of spectroscopic investigations of silicate melts at elevated temperatures has now aided considerably in placing the relaxation behavior of silicate melts on an atomistic basis. Simple observations have, for some time, implied a relationship between atomic mobility, diffusion, and viscosity. Experimental advances in the obtainment of diffusivity and viscosity

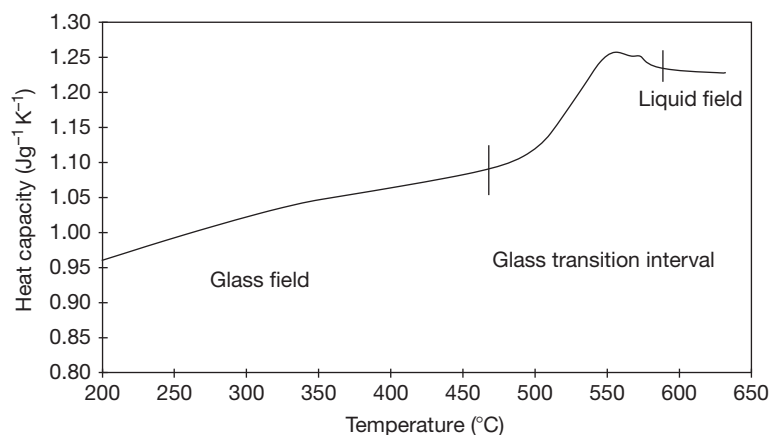


Figure 2 Phenomenology of the glass transition. The heat capacity of a silicate melt expresses a temperature-dependent glassy segment at lower temperature, a higher segment in the liquid state at higher temperature and a hysteresis in the glass transition interval whose path links the two states – glassy and liquid. The increase in heat capacity at the glass transition results from the self-diffusion of atoms in the structure, which enables temperature-dependent configurational changes in the structure to follow their temperature-dependent equilibria. In the glass, such reactions are largely frozen out.

data have led to the somewhat paradoxical confirmation of Stokes–Einstein or Eyring formulations of viscosity–diffusivity relationships for certain chemical components of silicate melts (Shimizu and Kushiro, 1984) under certain conditions yet rejection for others (e.g., Hofmann, 1980; Jambon, 1982). We now know that the picture of atomistic origins of relaxation clearly must distinguish between individual chemical components of the melt phase such that some components appear to control the relaxation responsible for determining the rheology of the melt (Si and O) and others do not (Li and Na). These relations are possibly best illustrated with the aid of a so-called relaxation map of all available atomistic mobility information for a particular melt composition (Figure 3).

2.19.3 Diffusion in Melts

2.19.3.1 Fundamental Concepts

Diffusion reflects temperature and establishes chemical equilibrium. It is the fundamental diffusive mobility of atoms in materials at temperature that is ultimately responsible for the achievement of equilibrium in chemical reactions, for the re-equilibrative response by relaxation of a system or phase to a perturbation of its thermodynamic state, and for the maintenance through time of the state of equilibrium by dynamic diffusive exchange of atoms/bonds. As such, diffusion is at the heart of the establishment and maintenance of equilibrium.

2.19.3.2 Methods of Investigation

Information on the magnitude of diffusivities in silicate melts comes from a range of experimental approaches, both direct and indirect (Chakraborty, 1995).

Direct determinations of diffusivity in silicate melts have been dominated by studies involving the microanalytical determination of experimentally generated gradients in either isotopic or chemical concentration. A range of experimental geometries has been employed including cylindrical half-space

couples, sphere absorption/desorption, thin source, and others. All of these techniques rely upon the spatial resolution of chemical or isotopic gradients that have usually been induced via annealing of an initial step function concentration gradient over time. As such, time series form the strategy surrounding the central experimental variable of time. Combined with variations in pressure and temperature, the diffusivity and its temperature and pressure dependence are mapped out for the silicate melt. Variation of further field variables, such as electric field, has been pursued in the materials literature but has played no significant role in the investigations within the geoscientific community.

Direct derivation of self-diffusivities via relaxation techniques in spectroscopy has also played a role in our understanding of silicate mobility. Motional averaging of individual species, for example, has yielded diffusivity estimates for cations in silicate melts.

As discussed in the preceding text, viscosity–diffusivity relationships have been elaborated for silicate melts with the result that diffusivities can be inferred from viscosities for selected components in silicate melts. As the viscosity database far outweighs the diffusivity database for which those relationships apply, this method of indirect determination of diffusivity via viscosity determination or relaxation behavior has not been exploited significantly in the geoscientific literature.

2.19.3.3 Tracer Diffusivities, Self-Diffusivities, and Chemical Diffusion

It is essential at the outset of thinking about diffusion in melts to distinguish between self-diffusion on the one hand and chemical diffusion on the other. The self-diffusion of a component occurs in the absence of chemical gradients. The chemical diffusion of a component occurs in the presence of and in response to a gradient in its chemical potential expressed as a concentration gradient in the host phase. The simplest consequence is that chemical diffusion is directed, whereas self-diffusion is not. The most common approach to the

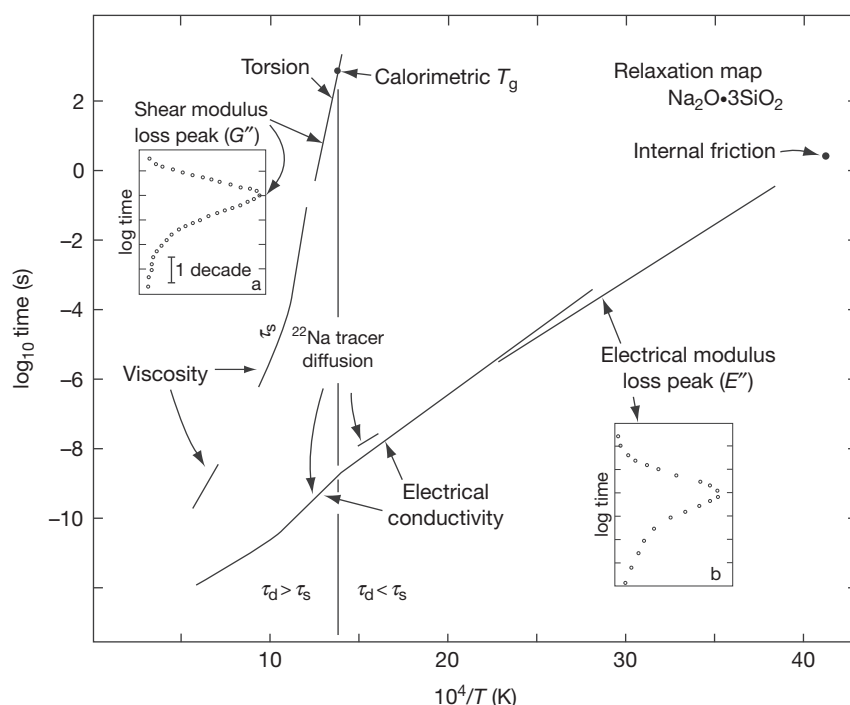


Figure 3 A relaxation map for a sodium silicate melt. Various experimental data sources on differing melt properties (mechanical, calorimetric, and electric) are combined and compared with each other in order to obtain an overview of the relaxational landscape and locations of relaxational modes, within the silicate melt structure. Two fundamental relaxation modes are seen here – a slow one related to Si mobility and a faster one related to Na mobility. Adapted from Dingwell DB (1995) Relaxation in silicate melts: Some applications in petrology. In: Stebbins JF, Dingwell DB, and McMillan PF (eds.) *Structure, Dynamics and Properties of Silicate Melts*, Vol. 32: *Reviews in Mineralogy*, pp. 21–66. Washington, DC: Mineralogical Society of America; Dingwell DB (1995) Viscosity and Anelasticity of melts and glasses. In: Ahrens T (ed.) *Mineral Physics and Crystallography: A Handbook of Physical Constants*, Vol. 2: *AGU Reference Shelf*, pp. 209–217. Washington, DC: American Geophysical Union, with permission.

determination of self-diffusion in silicate melts has been via isotopic doping in diffusion couples. Tracer diffusion typically describes diffusion of a species in the presence of a minimal activity gradient. Although in principle, anything detectable can be considered as a tracer in such a system, the phrase tracer diffusion usually refers to a trace element concentration level doping of a system and the subsequent spatial resolution of its chemical diffusion. At very low levels of concentration, the inference is sometimes made that tracer diffusion can approach the value of self-diffusion in the system.

In general, self-diffusivities and chemical diffusivities are different in magnitude and cannot be compared for the purpose of deriving relative structural information about the diffusion matrix, the silicate melt. Self-diffusivities contain fundamental information on the silicate melt structure and/or the structural role of the diffusing species. Chemical diffusivities contain information on the activity–composition relationships of the diffusing species in the host melts.

2.19.3.4 Temperature and Pressure Dependence of Diffusion

The temperature dependence of diffusivities in silicate melts at high temperature is most commonly described via an Arrhenius relationship (i.e., a logarithmic dependence of a property upon the reciprocal of absolute temperature). This situation is certainly valid for the typically restricted ranges of temperature involved in high-temperature determinations of diffusivities in

low-viscosity liquids. It is probably not valid for some species when observed over a larger temperature range (Dingwell, 1990). Arrhenius activation energies of diffusion range widely as a function of ionic properties, melt composition, and absolute temperature range. In the succeeding text, the potential complexity of the temperature dependence of diffusivities is discussed within the context of their relationship to viscosity.

The pressure dependence of diffusion is highly variable. At a given temperature and pressure range, it can be either positive or negative, depending on the identity of the ion. As a function of pressure, the pressure dependence of diffusivity may also switch from a positive to a negative pressure dependence (Poe and Rubie, 1998; Poe et al., 1997).

The structural basis for the interpretation of the temperature and, especially, the pressure dependence of diffusivities is far from complete. General relationships of the temperature dependence are discussed in more detail in the succeeding text. General aspects of the pressure dependence are given to date in very broad terms in the literature, usually without direct structural data to confirm them. Progress is badly needed here if we are to develop truly generalizable relationships.

2.19.3.5 Concentration-Dependent Diffusion

Concentration dependence of diffusivity in silicate melts has been demonstrated for several components. Systems exhibiting concentration-dependent diffusivity possess, by definition, significant activity and thus concentration gradients. Diffusion in

the presence of such chemical concentration gradients is chemical diffusion. Thus, concentration dependence of diffusivities can be viewed as the case where the compositional dependence of the chemical diffusivity of the diffusing speciation is approximated by the incorporation of a single compositional gradient, that of the diffusing species itself. One of the best established cases of the approximation of concentration-dependent diffusivity is that of H_2O in rhyolitic melts (Behrens et al., 2004).

2.19.3.6 Intrinsic Versus Extrinsic Diffusivities

The relationship between viscosity and diffusivity may be well illustrated using the abundant data now available on the tracer and/or self-diffusivity of various cations in multicomponent silicate melts for which the viscosity may be calculated. This is attempted in Figures 4 and 5. Cationic diffusivities are plotted versus melt viscosity for a range of multicomponent silicate

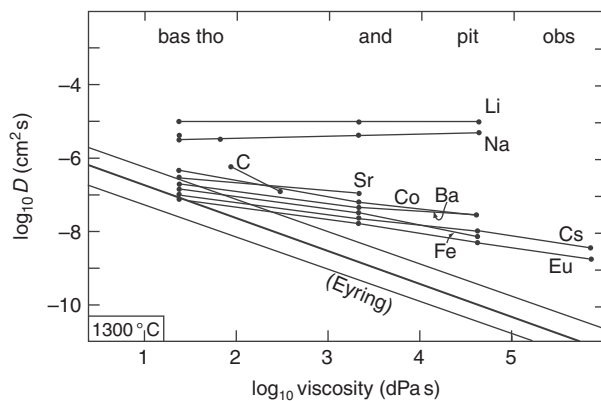


Figure 4 Tracer diffusion data plotted versus the estimated viscosity of the host melt. With the exception of the fast cations, Na and Li, the diffusivities of all others cluster near the calculated Si diffusivity. These are defined as extrinsic diffusivities. Reproduced from Dingwell DB (1990) Effects of structural relaxation on cationic tracer diffusion in silicate melts. *Chemical Geology* 82: 209–216, with permission.

melts. The diffusivities of a structurally highly diverse range of cations can be seen to exhibit very similar values of diffusivity and its temperature dependence. Two cations (Na and Li) appear to form exceptions to the rule, exhibiting distinctly higher diffusivities. It is important to note that the viscosity dependence, and through it the composition dependence, of the cationic diffusivities is negative for the large grouping of cations clustered at lower diffusivity values but positive for the cations of higher diffusivity. Without any further constraints, diffusivity, as an expression of structure in these melts, appears paradoxical. The cations of lower diffusivity appear to behave independently of their cationic properties. C and Cs, two cations of extremely different cationic properties, have virtually identical diffusivities. There is however a further constraint, and that is the diffusivity of Si. It may be reliably estimated through the Stokes–Einstein relationship to lie, as represented in Figures 4 and 5, just at the base of the cluster of slower cationic diffusivities. In fact, the relative location of the Si diffusivity led Dingwell (1990) to suggest that the values of diffusivity being expressed by most of the cations in Figure 4 are controlled by the viscosity of the melt itself. These were termed then ‘extrinsic diffusivities.’ They are subequal for all such affected cations, there being only one value of viscosity at a given composition and temperature. Extrinsic diffusivities have in addition relatively high activation energies and are necessarily sensitive to any change in melt viscosity induced in the system.

The Na and Li data are, if joined by further data from melts of higher viscosity (Figure 5), shown to be a second class of diffusivities with respect to structural relaxation, such that cations exhibiting extrinsic diffusivities in very low-viscosity melts exhibit the alternative behavior of Na and Li in more viscous melts. These diffusivities, characterized by low activation energies, higher diffusivities than Si, and an insensitivity to melt viscosities, were termed ‘intrinsic diffusivities.’ Intrinsic diffusivities were so named as their striking variation in magnitude and activation energy appears to reflect their individual cationic properties quite rationally.

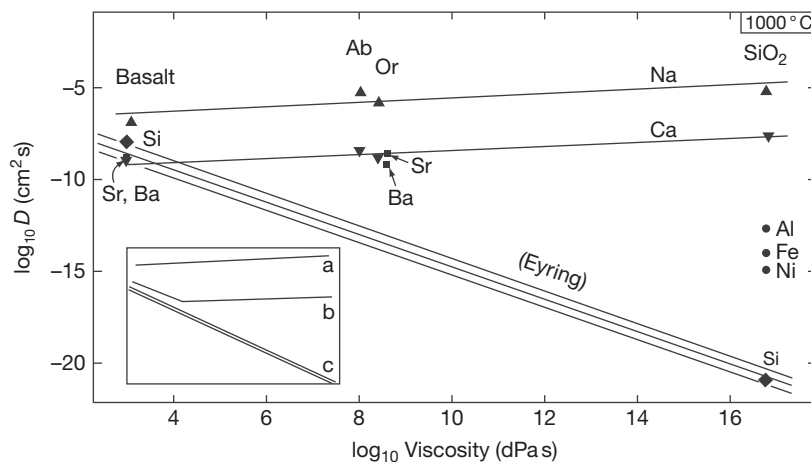


Figure 5 An expanded version of Figure 4 where additional data on the diffusivity of cations is plotted versus viscosity of the host melt. Here, intrinsic diffusivities can be distinguished clearly from extrinsic diffusivities. Perhaps, the simplest aspect of the distinction is the opposing viscosity dependence of intrinsic (positive) versus extrinsic (negative) diffusivities. Reproduced from Dingwell DB (1990) Effects of structural relaxation on cationic tracer diffusion in silicate melts. *Chemical Geology* 82: 209–216, with permission.

2.19.4 Melt Rheology

2.19.4.1 Methods of Investigation

The experimental measurement of silicate melt viscosity has a history going back a century. Studies directly dedicated to the Earth sciences have been performed for almost as long (e.g., Kozu and Kani, 1935). Inferences were drawn from such studies from the very start regarding their geologic and geophysical application (Bowen, 1934). Elevated pressures and temperatures were employed very early (see Dingwell, 1998b). Such studies and fundamental constraints on volcanism and magmatism were derived. This long history, together with the observation that melt viscosity ranges over more than ten orders of magnitude, has resulted in the application of a remarkable range of experimental methods for the investigation of melt viscosity (Figure 6). In principle, viscosity is determined either by setting the rate of deformation (strain rate) and obtaining the stress sustained by the liquid against its deformation or by setting the applied stress and obtaining the deformation rate of the sample.

2.19.5 Viscosity of Liquids

2.19.5.1 Newtonian Rheology in Silicate Melts

The Newtonian nature of the viscosity of silicate liquids has been extensively investigated. It is standard practice in the most common methods of viscometry employed for silicate liquids to systematically vary the strain rate during measurement in order to test for non-Newtonian behavior. It is safe to say that on the basis of the considerable viscosity dataset available today, the vast majority of melt deformation and transport processes within the deep Earth are likely to occur in the presence of a melt phase exhibiting purely Newtonian

behavior. The issue of the boundaries of Newtonian behavior in the laboratory has been investigated extensively. Toward the low strain rate side, the boundaries have not been found. We infer that they do not exist. Thus, there is no experimental evidence of yield strengths for liquid silicates. Toward the high strain rate side, the boundary of Newtonian behavior, or the so-called onset of non-Newtonian behavior, has been found, as described in detail in the succeeding text.

2.19.5.2 Temperature Dependence of Newtonian Viscosity

The temperature dependence of the viscosity of silicate melts may be expressed over limited temperature intervals as an exponential function of inverse absolute temperature.

In this so-called Arrhenius description, the temperature dependence is reflected in the magnitude of a coefficient commonly referred to as the activation energy of viscous flow. By analogy to rate theory, the activation energy was traditionally interpreted as reflecting an average energy barrier to flow. The temperature dependence of viscosity of several melts is illustrated in Figure 7, where the variation in activation energy at a given temperature is reflected in the range of slope values. The activation energy of geologic melts varies, at superliquidus temperatures from ~ 30 to 70 kcal mol^{-1} .

Inspection of Figure 7 readily reveals that the temperature dependence of the viscosity of silicate melts is, in general, non-Arrhenius. The temperature dependence increases with decreasing temperature, to a greater or lesser extent, for all melt compositions. This aspect of the temperature dependence of viscosity is most commonly expressed in terms of the addition of a term to the temperature dependence that effectively reduces the reciprocal absolute temperature. This empirical description

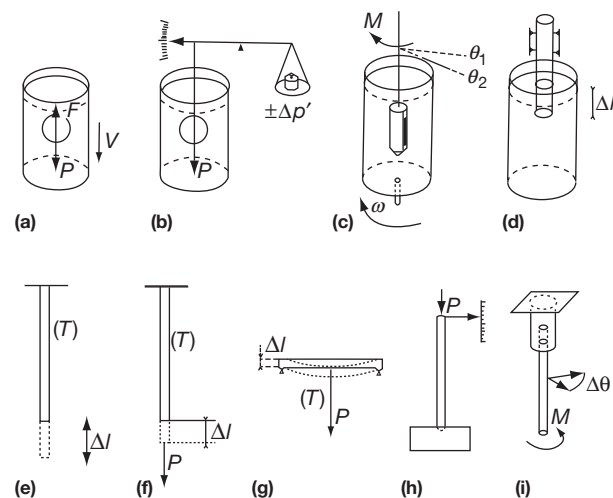


Figure 6 Geometric arrangements for experimental strategies of the determination of viscosity. Viscosity experiments may be grouped into two classes – those in which the stress is controlled and the strain rate monitored and those in which the strain rate is controlled and the resultant stress is monitored. Reproduced from Zarzycki J (1991) *Glasses and the Vitreous State*, 505 pp. Cambridge: Cambridge University Press, with permission.

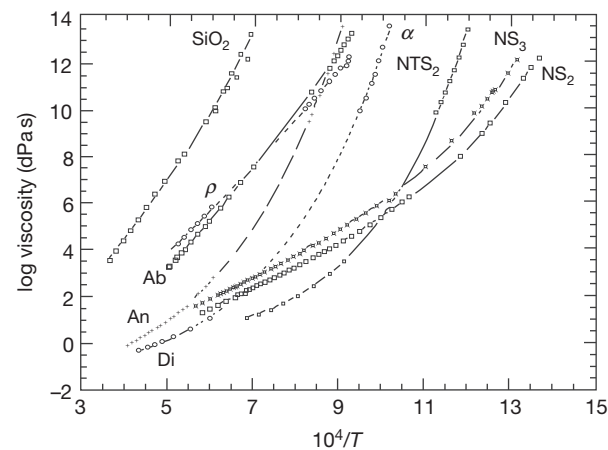


Figure 7 The non-Arrhenius nature of the temperature dependence of the Newtonian viscosity of silicate melts as exhibited by several analog compositions of relevance to geologic processes. The general trend toward more fragile behavior at lower absolute temperatures for a constant viscosity is evident. Ab, albite melt; Di, diopside melt; NTS₂, sodium titanosilicate melt; NS₃, sodium trisilicate; NS₂, sodium disilicate. Reproduced from Richet P and Bottinga Y (1995) *Rheology and configurational entropy of silicate melts*. In: Stebbins JF, Dingwell DB, and McMillan PF (eds.) *Structure, Dynamics and Properties of Silicate Melts, Vol. 32: Reviews in Mineralogy*, 616 pp. Washington, DC: Mineralogical Society of America, with permission.

of temperature-dependent melt viscosities using the Tammann–Vogel–Fulcher formulation, despite providing a good description of the data, lacks a theoretical basis.

A theoretical basis underlies the Adam and Gibbs (1965) formulation of viscous flow (based on cooperative relaxation) by Richet (1984). Here, the viscosity is expressed as an inverse function of the configurational entropy of the silicate melt. Adam–Gibbs theory holds the promise of a link between external thermodynamic properties of the silicate melt phase and its flow behavior. As such, it has been analyzed experimentally by comparison of calorimetric and rheological data for model silicates. The results for diopside liquid are presented in Figure 8 where the linearization of the temperature dependence of melt viscosity via a normalization to the temperature-dependent value of the configurational entropy (Richet et al., 1986).

2.19.5.3 Pressure Dependence of Newtonian Viscosity

The pressure dependence of the viscosity of silicate melts has been investigated predominantly in the low-viscosity regime at relatively high temperatures, typically above the high-pressure liquidus of the melts (Kushiro, 1976; Kushiro et al., 1976;

Scarfe et al., 1987; Wolf and McMillan, 1995). Such investigations have been based chiefly on falling sphere viscometry using Stokesian principles (see review by Dingwell, 1998b). Figure 9 contains a collection of pressure-dependent viscosity curves. The complexity of these trends implies that we do not yet have the proper structural information necessary for describing the pressure-induced change in flow mechanisms in silicate melts at high temperature in a systematized fashion. Undoubtedly, some surprises lie ahead.

2.19.5.4 Compositional Dependence of Newtonian Viscosity

The database on compositional dependence of Newtonian viscosity is vast. The salient features are summarized here. Figure 10 illustrates the relative viscosities of alkali- and alkaline-Earth aluminosilicate melts over a wide range of silica contents. It can be seen that the relative viscosities of these systems do not change and that the viscosity increases with decreasing field strength of the network stabilizing cation. This has been interpreted as a consequence of the relative mean bonds strengths in these tectosilicate liquids. Further, the fundamental feature of nonlinear compositional variation of

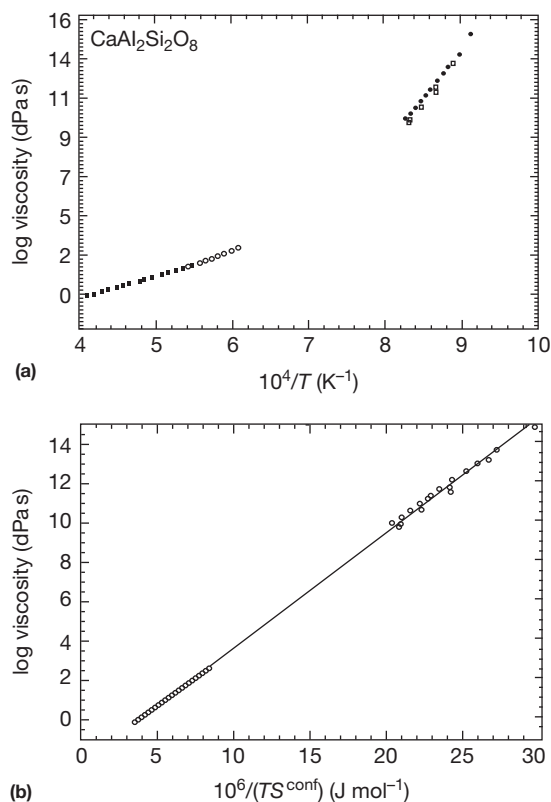


Figure 8 The normalization of the non-Arrhenius temperature dependence of the viscosity of diopside melt using calorimetrically derived data for the temperature dependence of the configurational entropy of the glass and liquid. Reproduced from Richet P, Robie RA, and Hemmingway BS (1986) Low temperature heat capacity of diopside glass ($\text{CaMgSi}_2\text{O}_6$) a calorimetric test of the configurational entropy theory applied to the viscosity of silicate liquids. *Geochimica et Cosmochimica Acta* 50: 1521–1533, with permission.

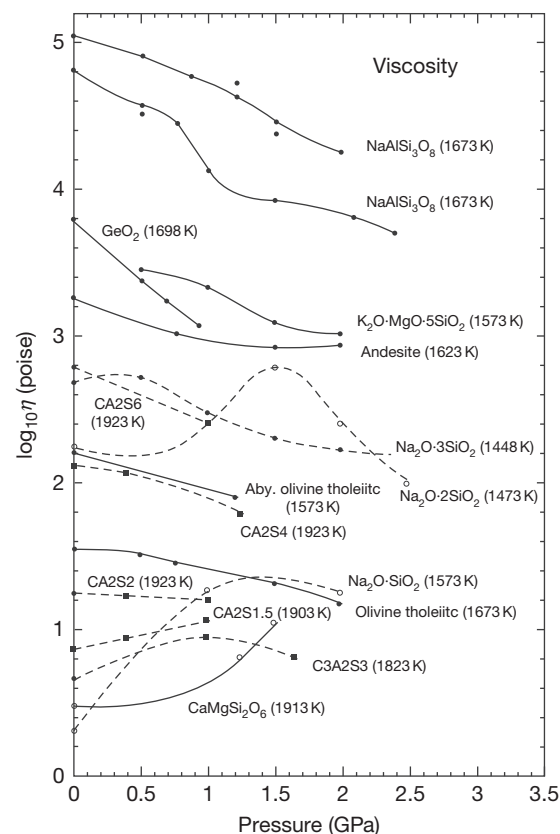


Figure 9 The pressure dependence of the Newtonian viscosity of silicate melts. The data are largely derived from Stokesian settling experiments. Adapted from Scarfe CM, Mysen BO, and Virgo DL (1987) Pressure dependence of the viscosity of silicate melts. *Geochemical Society, Special Publication No. 1*, pp. 59–67; Wolf GH and McMillan PF (1995) Pressure effects on silicate melt properties. *Reviews in Mineralogy* 32: 505–561, with permission.

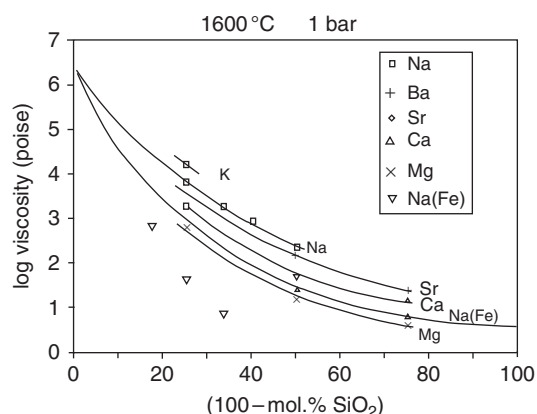


Figure 10 Systematics of the composition dependence of high-temperature melt viscosity in the alkali- and alkaline-earth aluminosilicate joins of nominal tectosilicate stoichiometry. Reproduced from Dingwell DB (1989) Shear viscosities of ferrosilicate liquids. *American Mineralogist* 74: 1038–1044.

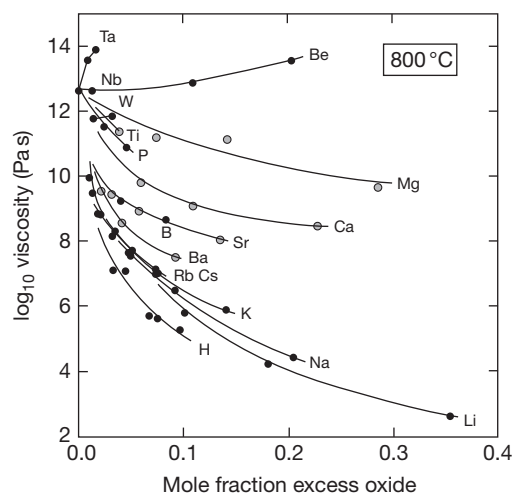


Figure 11 The comparative influences of over 20 components on the viscosity of a leucogranitic melt. These data are derived from new dilatometer-based techniques for the determination of high-viscosity melt properties at low temperatures. Reproduced from Dingwell DB (1997) The brittle-ductile transition in high-level granites: Material constraints. *Journal of Petrology* 38: 1635–1644, with permission.

viscosity is underlined by the curvature of the viscosity trends with decreasing silica content.

Coming from this relatively simple and ordered picture of the composition dependence of viscosity, we can obtain an impression of the variation in viscosity generated by melt composition from Figure 11 where the individual influences of a large number of components on the viscosity of a haplogranitic melt are illustrated. The influence of a further variable in melt composition; oxidation state on melt viscosity is summarized for several ternary silicate melts in Figure 12. Reduction of Fe-bearing melts results in a nonlinear decrease in viscosity. The viscosities of highly oxidized melts are very sensitive to oxidation state, whereas moderately reduced melts are relatively insensitive.

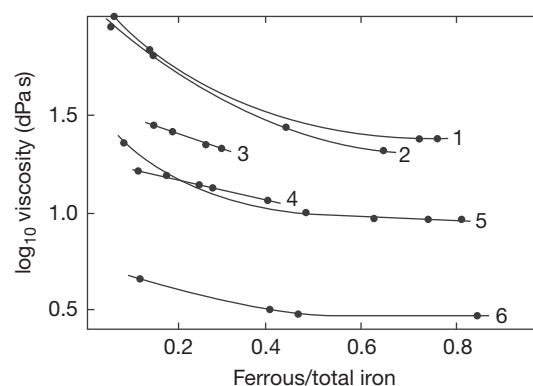


Figure 12 The influence of the redox state of iron on the viscosity of several ternary melts. A clear parameterization of the influence of redox on multicomponent melt viscosities remains outstanding at present. Reproduced from Dingwell DB (1991) Redox viscometry of some iron-bearing silicate liquids. *American Mineralogist* 76: 1560–1562, with permission.

The first non-Arrhenius model for geologically relevant melt compositions was generated for the system cal-calkaline rhyolite (metaluminous haplogranite) – H₂O (Hess and Dingwell, 1996). Its parameterization illustrates all of the essential features of the addition of water to a multicomponent silicate melt (Figure 13). A decade ago, sufficient low-temperature data existed to enable the effective modeling of non-Arrhenius melt viscosity in multicomponent compositional space (Giordano and Dingwell, 2003; Giordano et al., 2006). Figure 14(a) illustrates an example of the compositional range of natural multicomponent melts investigated and their measured viscosities. The quality of multicomponent fitting is illustrated in Figure 14(b) where the measured versus predicted viscosities are compared over ten log units of the viscosity. Five years ago, the first fully comprehensive parameterization of the temperature-viscosity relationships of petrologically relevant melt compositions incorporating water and fluorine was developed (Giordano et al., 2008). Today, this parameterization has become the standard for viscosity modeling beyond haplogranitic compositions (Figure 15).

2.19.5.5 Non-Newtonian Rheology in Silicate Melts

The non-Newtonian viscosity has been accessed experimentally using longitudinal compression, simple shear, and elongation (Hessenkemper and Brückner, 1988; Manns and Brückner, 1988; Simmons and Simmons, 1989; Simmons et al., 1982, 1988; Webb and Dingwell, 1990a,b). The elongational results for natural nephelinitic, basaltic, andesitic, and rhyolitic melts are presented in Figure 16 as a function of strain rate. Also included is the estimated relaxational strain rate from the Maxwell relation. The offset between the onset of noticeable strain rate dependence of the viscosity and the relaxational strain rate is constant and independent of composition. Thus, normalization of the results to the relaxational strain rate generates a single master curve for the onset of non-Newtonian viscosity at high strain rates, independent of composition. Further, the results from compressive longitudinal, simple shear, and these elongational studies also adhere to a single master curve. Thus,

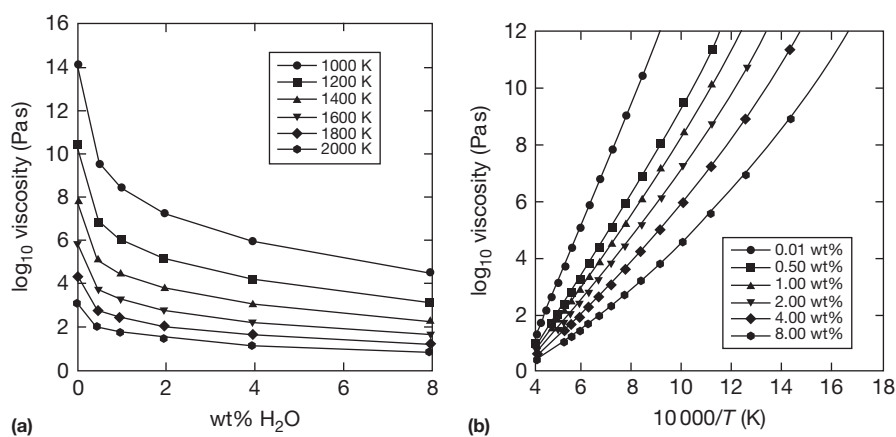


Figure 13 The temperature and water content dependence of the shear viscosity of haplogranitic melts. This parameterization was compiled using spectroscopic, volume, and shear stress relaxation data. Reproduced from Hess K-U and Dingwell DB (1996) Viscosities of hydrous leucogranitic melts: A non-Arrhenian model. *American Mineralogist* 81: 1297–1300, with permission.

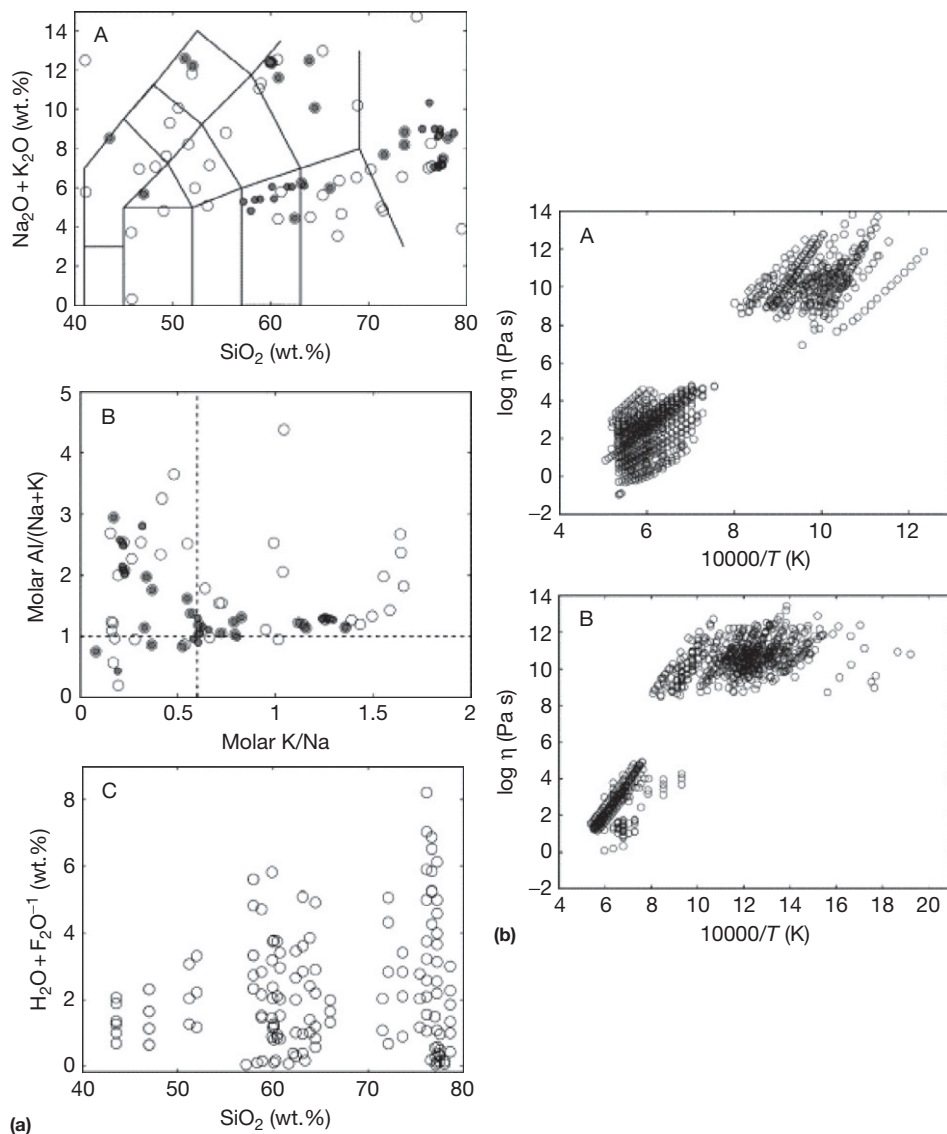


Figure 14 (Continued)

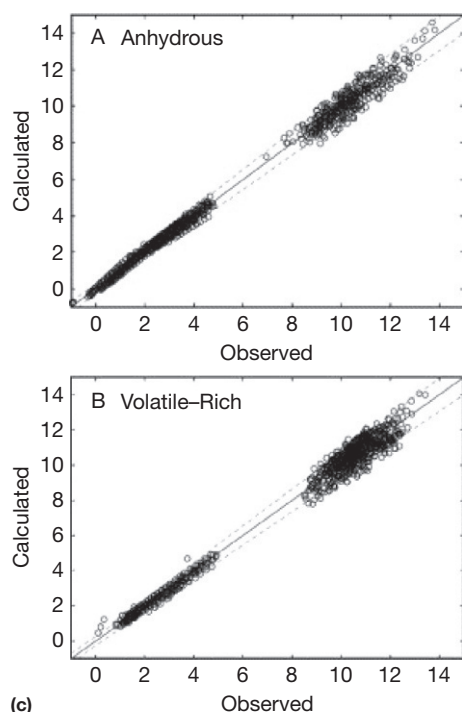


Figure 14 Cont'd (a) Melt compositions used in calibration of the GRD model for silicate melt viscosity, including volatile-free (open circles) and volatile-enriched (H_2O and F_2O^{-1}) melts. Melt compositions plotted as: (A) wt% SiO_2 vs. $\text{Na}_2\text{O} + \text{K}_2\text{O}$, (B) molar ratios of K/Na vs. $\text{Al}/(\text{Na} + \text{K})$, and (C) wt% SiO_2 vs. total volatile content. (b) Summary of data used by in the GRD model to calibrate VFT model for compositional dependence of silicate melt viscosity. Data shown as $\log \eta$ vs. $10\,000/T(\text{K})$ for (A) volatile-free, and (B) volatile-rich melts (Sources listed as supporting material in the Appendix). Note vertical axes are equivalent but horizontal axis for (B) has been extended to lower temperatures. (c) Results of the GRD model for the VFT-based model for compositional dependence of silicate melt viscosity. Observed values of viscosity are compared against model values for (A) anhydrous ($N = 932$ experiments) and (B) volatile-rich ($N = 842$ experiments) melts. Dashed lines indicate $\sim 5\%$ uncertainty on measured values of $\log \eta$. Reproduced from Giordano D, Russell JK, and Dingwell DB (2008) Viscosity of magmatic liquids: A model. *Earth and Planetary Science Letters* 271: 123–134.

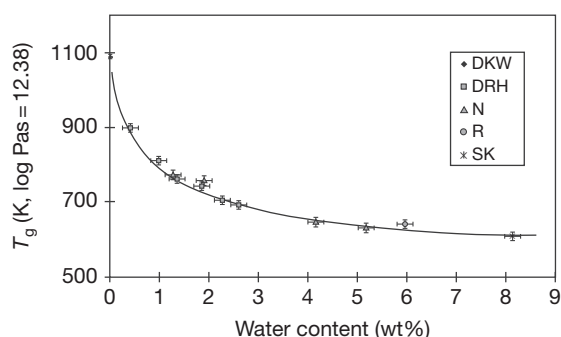


Figure 15 The variation of the glass transition temperature of hydrous granitic melts with water content as obtained by volume, shear stress, and structural relaxation studies. Reproduced with permission from Dingwell DB (1998) The glass transition in hydrous granitic melts. *Physics of the Earth and Planetary Interiors* 107: 1–8, where original data sources are listed.

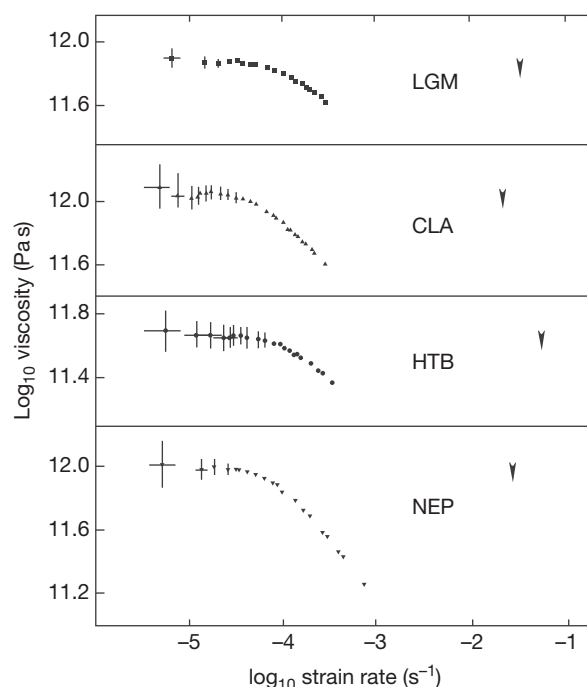


Figure 16 The onset of non-Newtonian rheology in geologic melts as determined using fiber elongation viscometry. LGM, Little Glass Mountain rhyolite; CLA, Crater Lake andesite; HTB, Hawaiian tholeiitic basalt; NEP, nephelinite. The deviation from Newtonian behavior occurs approximately 3 log units of strain rate below the relaxational strain rate (signified by the arrowheads). Reproduced from Webb SL and Dingwell DB (1990) Non-Newtonian rheology of igneous melts at high stresses and strain rates: Experimental results for rhyolite, andesite, basalt and nephelinite. *Journal of Geophysical Research* 95: 15695–15701, with permission.

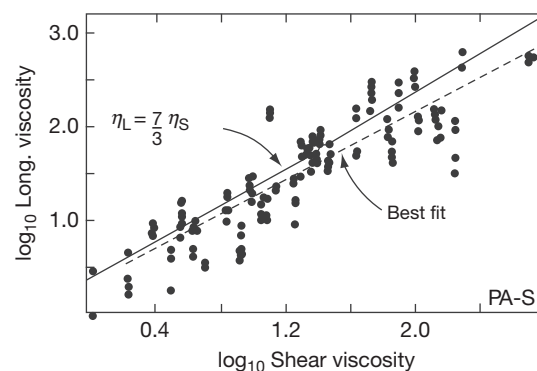


Figure 17 The equivalence of volume and shear viscosities of silicate melts demonstrated by the comparison of ultrasonically derived longitudinal viscosities with concentric cylinder-derived shear viscosities. Reproduced from Dingwell DB and Webb SL (1989) Structural relaxation in silicate melts and non-Newtonian melt rheology in igneous processes. *Physics and Chemistry of Minerals* 16: 508–516, with permission.

the tensorial properties of the strain do not influence the non-Newtonian onset significantly. In this context, it is noteworthy that the volume and shear viscosities of silicate melts are equal. In **Figure 17**, the assumption of an equivalence of the volume

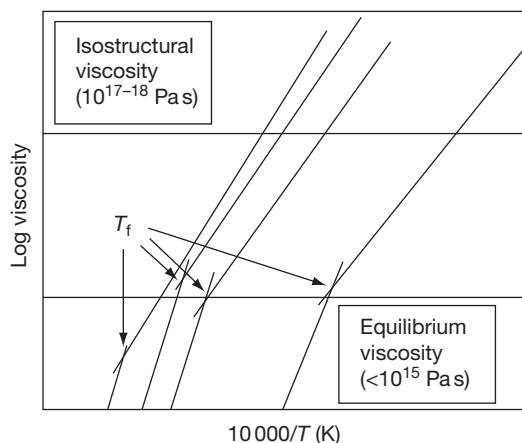


Figure 18 The relative temperature dependence of the equilibrium viscosity versus the isostructural viscosity. The temperature dependence of the equilibrium viscosity can be seen to be composed thereby from two contributions, one structural and one thermal, which are similar in magnitude. Reproduced from Dingwell DB (1995) Relaxation in silicate melts: Some applications in petrology. In: Stebbins JF, Dingwell DB, and McMillan PF (eds.) *Structure, Dynamics and Properties of Silicate Melts*, Vol. 32: *Reviews in Mineralogy*, pp. 21–66. Washington, DC: Mineralogical Society of America, with permission.

and shear viscosities is demonstrated to hold up well in the comparison of ultrasonically derived longitudinal viscosities and concentric cylinder-derived shear viscosities.

2.19.5.6 Isostructural Viscosity

Inherent in the temperature dependence of the viscosity of melts is that the thermal energy in the system and the configurational state of the liquid are both varying with temperature. Thus, the temperature dependence of the so-called equilibrium viscosity is a combination of effects. To obtain the temperature dependence of a single structured liquid, special loading–unloading experiments have been devised and conducted with the result that the activation energy sinks to about half its equilibrium value (Figure 18). This implies that about half of the temperature dependence of equilibrium viscosity is due to configurational changes in the structure of the melt and the other half is due to thermal energy increase in the individual bonds.

2.19.5.7 Failure of Melts

Incursions into the non-Newtonian flow of silicate melts are commonly terminated by melt failure. The non-Newtonian flow of the melt implies that the thermodynamic equilibrium structure of the melt cannot be maintained during viscous flow, generating a runaway process of structure collapse in the melt. The consequence of the collapse is shear thinning followed by melt failure. The stresses for these failures have been experimentally constrained and compared with estimates from other sources in the literature (Romano et al., 1996). The experimental observation of melt failure, together with its obvious significance for explosive volcanic eruptions, has in the meantime spawned a whole new field of investigation: experimental volcanology (Alidibirov and Dingwell, 1996a,b, 2000). To date, the essential character of melt failure and fragmentation

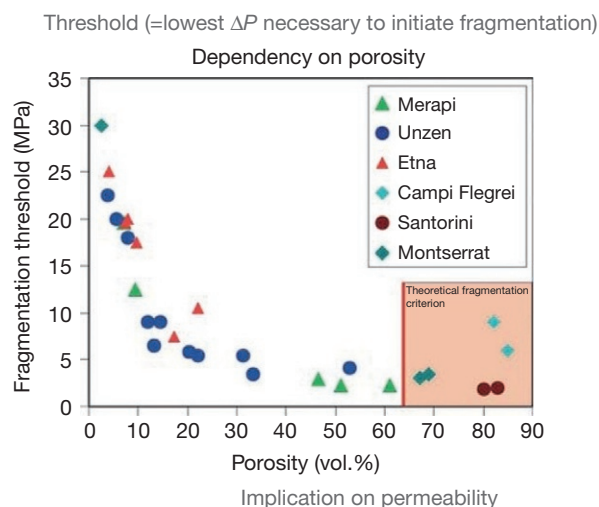


Figure 19 The fragmentation threshold of vesicular magma as a function of porosity. The fragmentation threshold is defined as the over pressure at which the magma will fail by fragmentation during rapid decompression. Reproduced from Spieler O, Kennedy B, Kueppers U, Dingwell DB, Scheu B, and Taddeucci J (2004) A fragmentation threshold for the initiation and cessation of explosive eruptions. *Earth and Planetary Science Letters* 226: 139–148, with permission.

has yielded quantifications of the fragmentation threshold (Figure 19; Spieler et al., 2004b), fragmentation speed (Scheu et al., 2005; Spieler et al., 2004a), fragmentation efficiency (Spieler et al., 2003; Kueppers et al., 2005 a,b), and the influence of permeability on these parameters (Mueller et al., 2005). The transition from flow to failure/fragmentation, which lies at the heart of major explosive eruptions (Dingwell, 1996), may even be a multiple, cyclic phenomenon on extruding high-viscosity lavas (Gonnermann and Manga, 2003; Tuffen and Dingwell, 2004; Tuffen et al., 2003) and thereby a central feature of magma ascent with significant implications for the kinematics of erupted magmas (Kennedy et al., 2005; Marti et al., 1999).

2.19.6 Concluding Statement

Rheology, viscosity, and transport lie at the heart of the significance of melt generation and transport in the evolution and behavior of our planet. Revised understanding of these transport properties in the past decade have led to fundamental corrections in our understanding of the liquid state and its behavior in natural processes. Equally, entirely new experimental branches have opened up due to the questions posed by this revised appreciation of diffusion, viscosity, and flow of melts.

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2.20 Seismic Anisotropy of the Deep Earth from a Mineral and Rock Physics Perspective

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2.20.1 Introduction

Seismic anisotropy is commonly defined as the direction-dependent nature of the propagation velocities of seismic waves. However, this definition does not cover all the seismic manifestations of seismic anisotropy. In addition to direction-dependent velocity, there is direction-dependent polarization of P- and S-waves, and anisotropy can contribute to the splitting of normal modes. Seismic anisotropy is a characteristic feature of the Earth, with anisotropy being present near the surface due to aligned cracks (e.g., Crampin, 1984), in the lower crust, upper mantle, and lower mantle due to mineral preferred orientation (e.g., Karato, 1998; Mainprice et al., 2000). At the bottom of the lower mantle in the D'' layer (e.g., Kendall and Silver, 1998), and in the solid inner core (e.g., Ishii et al., 2002a), the causes of anisotropy are still controversial (Figure 1). In some cases, multiple physical factors could be contributing to the measured anisotropy, for example, mineral crystal preferred orientation (CPO) and alignment of melt inclusions at mid-ocean ridge systems (e.g., Mainprice, 1997). In the upper mantle, the pioneering work of Hess (1964) and Raitt et al. (1969) from Pn velocity measurements in the shallow mantle of the ocean basins showed azimuthal anisotropy in a shallow horizontal layer. Long-period surface waves studies (e.g., Montagner and Tanimoto, 1990; Nataf et al., 1984) have since confirmed that azimuthal anisotropy and SH/SV polarization anisotropy are global phenomena in the Earth's upper mantle, particularly in the top 200 km of the upper mantle. Anisotropic global

tomography, based on surface and body wave data, has shown that anisotropy is very strong in the subcontinental mantle and present generally in the upper mantle, but significantly weaker at greater depths (e.g., Beghein et al., 2006; Panning and Romanowicz, 2006). The large wavelengths used in long-period surface wave studies mean that such methods are insensitive to heterogeneity less than the wavelength of about 1000 km. In an effort to address the problem of regional variations of anisotropy, the splitting of SKS teleseismic shear waves that propagate vertically has been extensively used. At continental stations, SKS studies show that the azimuth of the fast polarization direction is parallel to the trend of mountain belts (Fouch and Rondenay, 2006; Kind et al., 1985; Silver, 1996; Silver and Chan, 1988, 1991; Vinnik et al., 1989). From the earliest observations, it was clear that the anisotropy in the upper mantle was caused by the CPO of olivine crystals induced by plastic deformation related to mantle flow processes at the geodynamic or plate tectonic scale.

The major cause of seismic anisotropy in the upper mantle is the CPO caused by plastic deformation. Knowledge of the CPO and its evolution require well-characterized naturally deformed samples, experimentally deformed samples, and numerical simulation for more complex deformation histories of geodynamic interest. The CPO not only causes seismic anisotropy but also records some aspects of the deformation history. Samples of the Earth's mantle are readily found on the surface in the form of ultramafic massifs and xenoliths in basaltic or kimberlitic volcanics and as inclusions in diamonds. However, samples from depths greater than 220 km

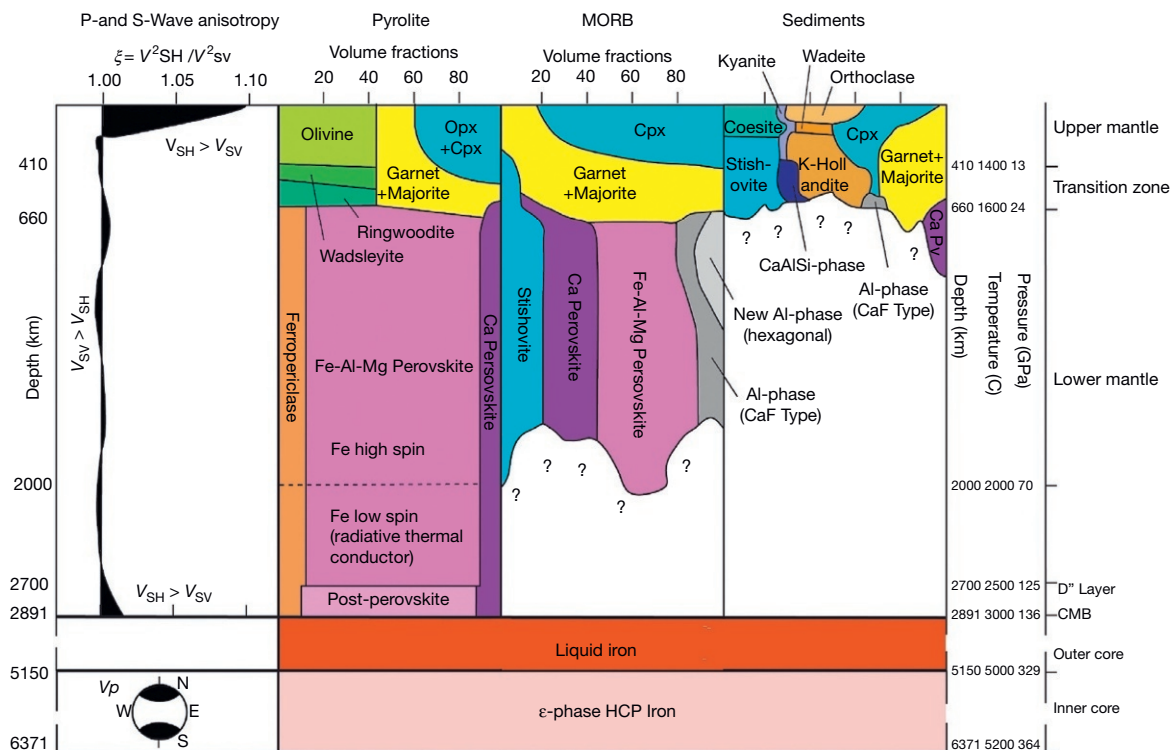


Figure 1 The simplified petrology and seismic anisotropy of the Earth's mantle and core. The radially (transverse isotropic) anisotropic model of S-wave anisotropy of the mantle is taken from [Panning and Romanowicz \(2006\)](#). The icon at the inner core represents the fast P-wave velocities parallel to the rotation axis of the Earth. The petrology of mantle is taken from [Ono and Oganov \(2005\)](#) for pyrolite and [Perrillat et al. \(2006\)](#) and [Ricolleau et al. \(2010\)](#) for the transformed MORB and based on [Irfune et al. \(1994\)](#) as modified by [Poli and Schmidt \(2002\)](#) for the transformed argillaceous sediments.

are extremely rare. Upper mantle samples large enough for the measurement of CPO have been recovered from kimberlitic volcanics in South Africa to a depth of about 220 km established by geobarometry (e.g., [Boyd, 1973](#)). Kimberlite mantle xenoliths of deeper origin (>300 km) with evidence for equilibrated majorite garnet, which is now preserved as pyrope garnet with exsolved pyroxene, have been reported ([Haggerty and Sautter, 1990](#); [Sautter et al., 1991](#)). It has been proposed that the Alpe Arami pyrope garnet lherzolite has been exhumed from a minimum depth of 250 km based on clinopyroxene exsolution lamellae present in diopside grains ([Bozhilov et al., 1999](#)). Samples of even deeper origin are preserved as inclusions in diamonds. Although most diamonds crystallize at depths of 150–200 km, some diamonds contain inclusions of majorite ([Moore and Gurney, 1985](#)), enstatite and ferropericlase ([Scott-Smith et al., 1984](#)), and $\text{CaSiO}_3 + (\text{Fe,Mg})\text{SiO}_3 + \text{SiO}_2$ ([Harte and Harris, 1993](#)). The mineral associations imply transition zone (410–660 km) and lower mantle origins for these diamond inclusions ([Kesson and Fitz Gerald, 1991](#)). Although these samples help to constrain mantle petrology, they are too small to provide information about CPO. Hence, knowledge of CPO in the transition zone, lower mantle, and inner core will be derived from deformation experiments at high pressure and temperature (e.g., olivine ([Couvry et al., 2004](#)), ringwoodite ([Karato et al., 1998](#)), perovskite ([Cordier et al., 2004b](#)), MgGeO_3 postperovskite ([Merkel et al., 2006a](#)), and ϵ -phase iron ([Merkel et al., 2005](#))).

It has been accepted since the PREM seismic model (Dziewoński and Anderson, 1981) that the top 200 km of the

Earth's mantle is anisotropic on a global scale (Figure 1). However, there are exceptions, for example, under the Baltic shield, the anisotropy increases below 200 km (Pedersen et al., 2006). The seismic discontinuity at about 200 km was first reported by the Danish seismologist Lehmann (1959, 1961), which now bears her name. However, the discontinuity is not always present at the same depth. Anderson (1979) interpreted the discontinuity as the petrologic change of garnet lherzolite to eclogite. More recently, interpretations have favored an anisotropy discontinuity, although, even this is controversial (see Vinnik et al., 2005), proposed interpretations include a local anisotropic decoupling shear zone marking the base of the lithosphere (Leven et al., 1981), a transition from an anisotropic mantle deforming by dislocation creep to isotropic mantle undergoing diffusion creep (Karato, 1992), simply the base of an anisotropic layer beneath continents (e.g., Gaherty and Jordan, 1995), or the transition from [100] to [001] direction slip in olivine (Mainprice et al., 2005). Global tomography studies show that the base of the anisotropic subcontinental mantle may vary in depth from 100 to 450 km (e.g., Polet and Anderson, 1995), but most global studies favor an anisotropy discontinuity for S-waves at around 200–250 km, which is stronger and deeper (300 km) beneath continents (e.g., Deuss and Woodhouse, 2002; Panning and Romanowicz, 2006; Ritsema et al., 2004) and weaker and shallower (200 km) beneath the oceans. There is also evidence for weak seismic discontinuities at 260 and 310 km that have been reported in subduction zones by Deuss and Woodhouse (2002).

A major seismic discontinuity at 410 km is due to the transformation of olivine to wadslevite (e.g., [Helffrich and](#)

Wood, 1996) with a shear wave impedance contrast of 6.7% (e.g., Shearer, 1996). The 410 km discontinuity has topography within 5 km of the global average. The olivine to wadsleyite transformation will result in the lowering of anisotropy with depth. Global tomography models (e.g., Beghein et al., 2006; Montagner, 1994a,b; Montagner and Kennett, 1996; Panning and Romanowicz, 2006) indicate that the strength of anisotropy is less in the transition zone (410–660 km) than in the upper mantle (Figure 1). A global study of the anisotropy of transition zone by Trampert and van Heijst (2002) has detected a weak anisotropy shear wave of about 1–2%. The surface wave overtone technique used by Trampert and van Heijst (2002) cannot localize the anisotropy within the 410–660 km depth range; however, the only mineral with a strong anisotropy and significant volume fraction in the transition zone is wadsleyite occurring between 410 and 520 km. Between 520 and 660 km, there is an increase in the very weakly anisotropic phases, such as garnet, majorite, and ringwoodite in the transition zone (Figure 1). Tommasi et al. (2004) had shown that the CPO predicted by a plastic flow model using the experimentally observed slip systems of wadsleyite can reproduce the weak anisotropy observed by Trampert and van Heijst (2002). The weaker discontinuity at 520 km, with a shear wave impedance contrast of 2.9%, has been reported by Shearer and coworkers (e.g., Flanagan and Shearer, 1998; Shearer, 1996). The discontinuity at 520 km depth has been attributed to the wadsleyite to ringwoodite transformation by Shearer (1996). Deuss and Woodhouse (2001) had reported the ‘splitting’ of the 520 km discontinuity into two discontinuities at 500 and 560 km, they interpreted the variations of depth of 520 km, and the presence of two discontinuities at 500 and 560 km in certain regions can only be explained by variations in temperature and composition (e.g., Mg/Mg+Fe ratio), which affect the phase transition Clapeyron. Regional seismic studies by Vinnik and coworkers (Vinnik and Montagner, 1996; Vinnik et al., 1997) show evidence for a weakly anisotropic (1.5%) layer for S-waves at the bottom 40 km of the transition zone (620–660 km). Some global tomography models (e.g., Montagner, 1998; Montagner and Kennett, 1996) also show significant transverse isotropic anisotropy in the transition zone with $V_{SH} > V_{SV}$ and $V_{PH} > V_{PV}$. Given the low intrinsic anisotropy of most of the minerals in the lower part of the transition zone, Karato (1998) suggested that this anisotropy is due to petrologic layering caused by garnet and ringwoodite rich layers of transformed subducted oceanic crustal material. Such a transversely isotropic medium with a vertical symmetry axis would not cause any splitting for vertically propagating S-waves and would not produce the azimuthal anisotropy observed by Trampert and van Heijst (2002), but would produce the difference between horizontal and vertical velocities seen by global tomography. A global study supports this suggestion, as high-velocity slabs of former oceanic lithosphere are conspicuous structures just above the 660 km discontinuity in the circum-Pacific subduction zones (Ritsema et al., 2004). A regional study by Wookey et al. (2002) also finds significant shear wave splitting associated with horizontally traveling S-waves, which is compatible with a layered structure in the vicinity of the 660 km discontinuity. However, recent anisotropic global tomography models do not show significant anisotropy in this depth range (Beghein et al., 2006; Panning and Romanowicz, 2006).

The strongest seismic discontinuity at 660 km is due to the dissociation of ringwoodite to perovskite and ferropericlase (Figure 1) with a shear wave impedance contrast of 9.9% (e.g., Shearer, 1996). The 660 km discontinuity has an important topography with local depressions of up to 60 km from the global average in subduction zones (e.g., Flanagan and Shearer, 1998). From 660 to 1000 km, a weak anisotropy is observed in the top of the lower mantle with $V_{SH} < V_{SV}$ and $V_{PH} < V_{PV}$ (e.g., Montagner, 1998; Montagner and Kennett, 1996). Karato (1998) attributed the anisotropy to the CPO of perovskite and possibly ferropericlase caused by plastic deformation in the convective boundary layer at the top of the lower mantle. In this depth range, Kawakatsu and Niu (1994) had identified a flat seismic discontinuity at 920 km with S to P converted waves with an S-wave velocity change of 2.4% in Tonga, Japan Sea, and Flores Sea subduction zones. They suggested that some sort of phase transformation thermodynamically controls this feature, or alternatively, we may suggest that it marks the bottom of the anisotropic boundary layer proposed by Montagner (1998) and Karato (1998). Reflectors in lower mantle have been reported by Deuss and Woodhouse (2001) at 800 km depth under North America and at 1050 and 1150 km beneath Indonesia; they only considered the 800 km reflector to be a robust result. Karki et al. (1997c) had suggested that the transformation of the highly anisotropic SiO_2 polymorph stishovite to CaCl_2 structure at 50 ± 3 GPa at room temperature may be the possible explanation of reflectivity in the top of the lower mantle. However, according to Kingma et al. (1995), the transformation would take place at 60 GPa at lower mantle temperatures in the range 2000–2500 K, corresponding to depth of 1200–1500 km, that is several hundred kilometers below the 920 km discontinuity. It is highly speculative to suggest that free silica is responsible for the 920 km discontinuity as a global feature as proposed by Kawakatsu and Niu (1994). Ringwood (1991) suggested that 10% stishovite would be present from 350 to 660 km in subducted oceanic crust and this would increase to about 16% at 730 km. Hence, in the subduction zones studied by Kawakatsu and Niu (1994), it is quite possible that significant stishovite could be present to 1200 km and may be a contributing factor to the seismic anisotropy of the top of the lower mantle. From 1000 to 2700 km, the lower mantle is isotropic for body waves or free oscillations (e.g., Beghein et al., 2006; Montagner and Kennett, 1996; Panning and Romanowicz, 2006). Karato et al. (1995) had suggested by comparison with deformation experiments of fine-grained analogue oxide perovskite that the seismically isotropic lower mantle is undergoing deformation by superplasticity or diffusive creep, which traditionally has been considered to not produce a CPO; this is now being challenged by recent experimental results (Miyazaki et al., 2013; Sundberg and Cooper, 2008). In the bottom of the lower mantle, the D'' layer (100–300 km thick) appears to be transversely isotropic with a vertical symmetry axis characterized by $V_{SH} > V_{SV}$ (Figure 1) (e.g., Kendall and Silver, 1996, 1998), which may be caused by CPO of the constituent minerals, shape preferred orientation of horizontally aligned inclusions, possibly melt (e.g., Berryman, 2000; Williams and Garnero, 1996) or core material. It has been suggested that the melt fraction of D'' may be as high as 30% (Lay et al., 2004). Seismology has shown that D'' is extremely heterogeneous as shown by globally high fluctuations of shear (2–3%) and compressional (1%) wave

velocities (e.g., Lay et al., 2004; Mégnin and Romanowicz, 2000; Ritsema and van Heijst, 2001), a variation of the thickness of D'' layer between 60 and 300 km (e.g., Sidorin et al., 1999a), P- and S-wave velocity variations sometimes correlated and sometimes anticorrelated (thermal, chemical, and melting effects?) (e.g., Lay et al., 2004), ultralow-velocity zones at the base of D'' with V_p 10% slower and V_s 30% slower than surrounding material (e.g., Garnero et al., 1998), and regions with horizontal (e.g., Kendall, 2000; Kendall and Silver, 1998) or inclined anisotropy (e.g., Garnero et al., 2004; Maupin et al., 2005; McNamara et al., 2003; Wookey et al., 2005a) in the range 0.5–1.5% and isotropic regions, localized patches of shear velocity discontinuity, that even predicted the possibility of a globally extensive phase transformation (Nataf and Houard, 1993) and its Clapeyron slope (Sidorin et al., 1999b). Until recently, the candidate phase for this transition was SiO_2 (Murakami et al., 2004). However, the mineralogical picture of the D'' layer has been completely changed with the discovery of postperovskite by Murakami et al. (2004), which is produced by the transformation of Mg-perovskite in the laboratory at pressures greater than 125 GPa at high temperature. Seismic modeling of the D'' layer using the new phase diagram and elastic properties of perovskite and postperovskite can explain many features mentioned earlier near the core-mantle boundary (Wookey et al., 2005b). The imaging of the layered structures within the D'' region by van der Hilst et al. (2007) using three-dimensional inverse scattering of core-reflected shear waves has provided a more quantitative view of D'' heterogeneity. The layered structures imaged by van der Hilst et al. (2007) are compatible with transverse isotropic anisotropy reported by earlier studies (e.g., Kendall, 2000; Kendall and Silver, 1998; Wookey et al., 2005a).

Although the outer core was discovered by British geologist Richard Oldham in 1906 (Oldham, 1906), the inner solid core was identified 30 years later by the Danish seismologist Inge Lehmann in a paper published in 1936 with the short title P'. She identified P-waves that traveled through the core region (PKP, where K stands for core) at epicentral distances of 105–142° in contradiction to the expected travel times for a single core model (Lehmann, 1936). She proposed a two-shell model for the core with a uniform velocity of about 10 km s⁻¹ with a small velocity discontinuity between each shell and an inner shell radius of 1400 km, close to the actually accepted value of 1221.5 km from PREM (Dziewoński and Anderson, 1981). The liquid nature of the outer core was first proposed by Jeffreys (1926) based on shear wave arrival times, and the solid nature of inner core was first proposed by Birch (1940) based on the compressibility of iron at high pressure. Given the great depth (5149.5 km) and the number of layers a seismic wave has to traverse to reach the inner core and return to the surface, it is not surprising that the first report of anisotropy of the inner core was inferred 50 years after the discovery of the inner core. Poupinet et al. (1983) were the first to observe that PKIKP (where K now stands for the outer core and I is for inner core) P-waves travel about 2 s faster parallel to the Earth's rotation axis than waves traveling the equatorial plane. They interpreted their observations in terms of a possible heterogeneity of the inner core. Shortly afterward, a PKIKP travel time study by Morelli et al., 1986 and normal modes (free oscillations) by Woodhouse et al. (1986) reported new observations

and interpreted the results in terms of anisotropy. However, the interpretation of PKIKP body wave travel times in terms of anisotropy remained controversial, with an alternative interpretation being that the inner core had a nonspherical structure (e.g., Widmer et al., 1992). Finally, the observation of large differential travel times for PKIKP for paths from the South Sandwich Islands to Alaska by Creager (1992) and Song and Helmberger (1993) and the interpretation of higher-quality free oscillation data by Tromp (1993, 1994) and Durek and Romanowicz (1999) gave further strong support for the homogenous transverse anisotropy interpretation. The general consensus became that the inner core is strongly anisotropic, with a P-wave anisotropy of about 3–4% with the fast velocity direction parallel to the Earth's rotation axis (see reviews by Creager, 2000; Song, 1997; Tromp, 2001). However, many studies have suggested variations to this simple anisotropy model of the inner core. It has been suggested that the symmetry axis of the anisotropy is tilted from the Earth's rotation axis (Creager, 1992; Shear and Toy, 1991; Su and Dziewoński, 1995) by 5–10°. A significant difference in the anisotropy between eastern and western hemispheres of the inner core has been reported by Creager (1999) and Tanaka and Hamaguchi (1997) with the western hemisphere having significantly stronger anisotropy than the eastern hemisphere that is nearly isotropic. Several recent studies concur that the outer part (100–200 km) of the inner core is isotropic and inner part is anisotropic (e.g., Garcia, 2002; Garcia and Souriau, 2000, 2001; Song and Helmberger, 1998; Song and Xu, 2002; Sun and Song, 2008). It has also been suggested that there is a small innermost inner core with radius of about 300 km with distinct transverse isotropy relative to the outermost inner core by Ishii and Dziewoński (2002). The innermost core has the slowest P-wave velocity at 45° to the east–west direction, and the outer part has a weaker anisotropy with slowest P-wave velocity parallel to the east–west direction. Using split normal mode constraints, Beghein and Trampert (2003) also showed that there is a change in velocity structure with radius in the inner core; however, their model shows that the symmetry of the P- and S-wave changes at about 400 km radius, suggesting a radical change, such as a phase transition of iron. Much of the complexity of the observations seems to be station- and method-dependent (see Ishii et al., 2002a,b). In a detailed study, Ishii et al. (2002a,b) derived a model that simultaneously satisfies normal mode, absolute travel time, and differential travel time data and has allowed them to separate a mantle signature and regional structure from global anisotropy of the inner core. Their preferred model of homogeneous transverse isotropy with a symmetry axis aligned with the rotation axis contradicts many of models proposed earlier but is similar to previous suggestions. In a study of inner core P-wave anisotropy using both finite-frequency and ray theories, Calvet et al. (2006) found that the data can be explained by three families of models that all exhibit anisotropy changes at a radius between 550 and 400 km (compared to 300 km for Ishii and Dziewoński (2002, 2003) and about 400 km for Beghein and Trampert (2003)). The first model has a weak anisotropy with a slow P-wave velocity symmetry axis parallel to the Earth's rotation axis. The second model has a nearly isotropic innermost inner core. Lastly, the third model has a strongly anisotropic innermost inner core with a fast symmetry

axis parallel to the Earth's rotation axis. These models have very different implications for the origin of the anisotropy and the history of the Earth's core. These divergences partly reflect the uneven sampling of the inner core by PKP(DF) paths resulting from the spatial distribution of earthquakes and seismographic stations. A recent study using high-quality, 2360 handpicked PKIKP arrival times is the largest database to be used for studying the inner core to date (Lythgoe et al., 2014). Lythgoe et al. found their data are best explained by significant hemispherical variations in anisotropy (east 0.5–1.5%; west 3.5–8.8%), with slow V_p direction at 57–61° to the rotation axis at all depths (Figure 2). Furthermore, there is no need for innermost inner core to explain their data, and they suggest that observations of an innermost inner core are an artifact from averaging over lateral anisotropy variations.

Theoretical studies of the process of generating the Earth's magnetic field through fluid motion of the outer core have predicted that the electromagnetic torque would force the inner core to rotate relative to the mantle (Glatzmaier and Roberts, 1995, 1996; Gubbins, 1981; Steenbeck and Helmig, 1975; Szeto and Smylie, 1984). Song and Richards (1996) first reported seismic differential travel time observations based on three decades of data supporting the eastward relative rotation of inner core by about 1° per year faster than the daily rotation of the mantle and crust; this is sometimes referred to as the superrotation of the inner core. Around the equator of the inner core, this rotation rate corresponds to a speed of a few tens of kilometers per year. The interpretation of the observed travel times required using the seismic anisotropy model inner core established by Su and Dziewoński (1995). Clearly, to establish such small relative rotation rate, a detailed knowledge of anisotropy, heterogeneity, and shape of the inner core is required, as travel times will change with direction and time (Song, 2000). The result was supported by some studies (e.g., Creager, 1997) and challenged by other studies (e.g., Souriau et al., 1997), but all indicated a smaller rotation rate than 1° per year. Zhang et al. (2005) reported a rotation rate of 0.3–0.5° using techniques that avoid artifacts of poor event locations and

contamination by small-scale heterogeneities. Tkalcic et al. (2013) found that rotation rate varies with time with mean values of 1° per year over a 10-year period and fluctuations of 0.25–0.48 per year. An analysis reconciling the hemispherical structure with the inner core superrotation, and avoiding the presence of innermost inner core, has been present by Waszek et al. (2011). The authors link the superrotation to the 3-D east-west hemispherical boundary structure and the eastward displacement of these boundaries with depth. In agreement with other studies suggesting the melting in the eastern hemisphere and crystallization in the west, which are responsible for the translation of the inner core towards the east (e.g., Alboussière et al., 2010; Monnereau et al., 2010). The estimated superrotation rate based on the eastward growth rate is extremely low at 0.1–1° per million years. If previously reported measurements of 0.3–0.5° per year are to be accepted, they can only represent short-term fluctuations of the rotation rate. Shear waves are very useful for determining the magnitude and orientation of anisotropy along individual ray paths; despite several claims to have observed shear waves (e.g., Julian et al., 1972; Okal and Cansi, 1998), the analysis of the attenuation (Doornbos, 1974) and frequency range (Deuss et al., 2000) reveals that these claims are unjustified. The analysis and validation of observations by Deuss et al. (2000) provide the first reliable observation of long-period (20–30 s) shear waves providing new possibilities for exploring the anisotropy of inner core. Wookey and Helffrich (2008) presented two observations of an inner core shear wave phase (PKJKP) at higher frequencies in stacked data from the Japanese high-sensitivity array (Hi-Net). Their model based on S-wave data is that c -axis of the hexagonal close-packed (hcp) iron phase is aligned normal to the Earth's rotation axis as proposed by Steinle-Neumann et al. (2001). As I will discuss later, it is not obvious that this interpretation is compatible with the majority of now available mineral physics data.

The transverse isotropy observed for P-waves traveling through the inner core could be explained by the CPO of the hcp form of iron (ϵ -phase) crystals or a layered structure. The

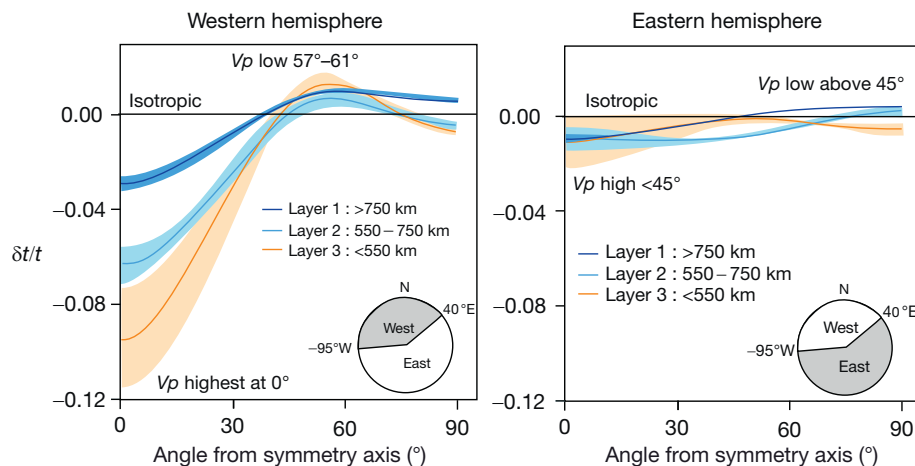


Figure 2 An anisotropy model for the eastern and western hemispheres of the inner core with hemispherical boundaries at 95°W and 40°E. Radial boundaries are at 750 and 550 km from the center of the Earth. The P-wave travel time residual ($\delta t/t$) is a perturbation of a weak cylindrical anisotropy from spherically symmetrical model given by Lythgoe et al. (2014). The angle from symmetry axis in this case is the angle between the ray path and the Earth's rotation axis. Isotropic elastic behavior is equivalent to $\delta t/t = 0$, indicated by the horizontal black line.

analysis of the coda of short-period inner core boundary-reflected P-waves (PKiKP) requires only a few percent heterogeneity at length scales of 2 km (Vidale and Earle, 2000), which suggests a relatively homogenous nonstructured inner core; however, this interpretation of coda has recently been questioned by Poupinet and Kennett (2004). The mechanism responsible for the CPO has been the subject of considerable speculation in recent years, with the suggested mechanisms including the alignment of crystals in the magnetic field as they solidify from the liquid outer core (Karato, 1993), the alignment of crystals by plastic flow under the action of Maxwell normal stresses caused the magnetic field (Karato, 1999), faster crystal growth in the equatorial region of the inner core (Yoshida et al., 1996), anisotropic growth driven by strain energy (Stevenson, 1987), dendritic crystal growth aligned with the direction of dominant heat flow (Bergman, 1997), plastic flow in a thermally convective regime (Jeanloz and Wenk, 1988; Wenk et al., 1988, 2000), and plastic flow under the action of magnetically induced Maxwell shear stresses (Buffett and Wenk, 2001). An alternative explication that was proposed by Singh et al. (2000) to explain the P-wave anisotropy and the low shear wave velocity of about 3.6 km s^{-1} (Deuss et al., 2000) is the presence of a volume fraction of 3–10% liquid iron (or FeS) in the form of oblate spherical inclusions aligned in the equatorial plane in a matrix of iron crystals with their c-axes aligned parallel to the rotation axis as originally proposed by Stixrude and Cohen (1995). The S-wave velocity and attenuation data are mainly from the outer part of the inner core, and hence, it was suggested the liquid inclusions are present in this region. Note that this is in contradiction with other studies, which suggest that the outer core has a low anisotropy. Several problems that are posed by all models to different degrees are the inner core thermally convective (see Stevenson, 1987; Weber and Machetel, 1992; Yukutake, 1998), the viscosity of the inner core, the strength of magnetic field and magnitude Maxwell stresses necessary to cause crystal alignment, the presence of liquids, and even the ability of the models to correctly predict the magnitude and orientation of the seismic P-wave anisotropy. Given the range of seismic models and the variety of physical phenomena proposed to explain these models, better contents on the seismic data, probably using better quality data and a wider geographic distribution of seismic stations in polar regions, are urgently required.

In this chapter, I review our current knowledge of the seismic anisotropy of the constituent minerals of the Earth's interior and our ability to extrapolate these properties to mantle conditions of temperature and pressure (Figure 1). I will begin by reviewing the fundamentals of elasticity, plane wave propagation in anisotropic crystals, the measurements of elastic constants, and the effective elastic constants of crystalline aggregates.

2.2.0.2 Mineral Physics

2.2.0.2.1 Elasticity and Hooke's Law

Robert Hooke's experiments demonstrated that extension of a spring is proportional to the weight hanging from it, which was published in *de Potentia Restitutiva* (or of Spring Explaining the Power of Springing Bodies (1678)), establishing that in elastic solids, there is a simple linear relationship between stress and

strain. The relationship is now commonly known as Hooke's law (*Ut tensio, sic vis* – which translated from Latin is 'as is the extension, so is the force' – was the solution to an anagram announced 2 years early in 'A Description of Helioscopes and some other Instruments 1676,' to prevent Hooke's rivals from claiming to have made the discovery themselves!). In the case of small (infinitesimal) deformations, a Maclaurin expansion of stress as a function of strain developed to first order correctly describes the elastic behavior of most linear elastic solids:

$$\sigma_{ij}(\epsilon_{kl}) = \sigma_{ij}(0) + \left(\frac{\partial \sigma_{ij}}{\partial \epsilon_{kl}} \right)_{\partial \epsilon_{kl}=0} \epsilon_{kl} + \frac{1}{2} \left(\frac{\partial^2 \sigma_{ij}}{\partial \epsilon_{kl} \partial \epsilon_{mn}} \right)_{\partial \epsilon_{kl}=0} \epsilon_{kl} \epsilon_{mn} + L$$

As the elastic deformation is zero at a stress of zero, then $\sigma_{ij}(0)=0$, and restricting our analysis to first order, then we can define the fourth-rank elastic tensor c_{ijkl} as

$$c_{ijkl} = \left(\frac{\partial \sigma_{ij}}{\partial \epsilon_{kl}} \right)_{\partial \epsilon_{kl}=0}$$

where ϵ_{kl} and σ_{ij} are, respectively, the stress and infinitesimal strain tensors. Hooke's law can now be expressed in its traditional form as

$$\sigma_{ij} = c_{ijkl} \epsilon_{kl}$$

The coefficients of the elastic fourth-rank tensor c_{ijkl} translate the linear relationship between the second-rank stress and the infinitesimal strain tensors. The four indexes ($ijkl$) of the elastic tensor have values between 1 and 3, so that there are $3^4=81$ coefficients. The stress tensor is symmetrical as we assume that stresses acting on opposite faces are equal and opposite, and hence, there are no stress couples to produce a net rotation of the elastic material. The infinitesimal strain tensor is also symmetrical, because we assume that pure and simple shear quantities are so small that their squares and products can be neglected. Due to the symmetrical symmetry of stress and infinitesimal strain tensors, they only have six independent values rather than nine for the asymmetrical case, and hence, the first two (i, j) and second two (k, l) indexes of the elastic tensor can be interchanged:

$$c_{ijkl} c_{jilk} \text{ and } c_{ijkl} = c_{ijlk}$$

The permutation of the indexes caused by the symmetry of stress and strain tensors reduces the number of independent elastic coefficients to $6^2=36$ because the two pairs of indexes (i, j) and (k, l) can only have six different values:

$$1 \equiv (1, 1) \quad 2 \equiv (2, 2) \quad 3 \equiv (3, 3) \quad 4 \equiv (2, 3) = (3, 2) \quad 5 \equiv (3, 1) \\ = (1, 3) \quad 6 \equiv (1, 2) = (2, 1)$$

It is practical to write a 6 by 6 table of 36 coefficients with two Voigt indexes m and n (c_{mn}) that have values between 1 and 6, whereas the representation of the c_{ijkl} tensor with 81 coefficients would be a printer's nightmare. The relation between the Voigt (mn) and tensor indexes ($ijkl$) can be expressed most compactly by

$$m = \delta_{ij}i + (1 - \delta_{ij})(9 - i - j) \text{ and } n = \delta_{kl}k + (1 - \delta_{kl})(9 - k - l)$$

where δ_{ij} is the Kronecker delta ($\delta_{ij}=1$ when $i=j$ and $\delta_{ij}=0$ when $i \neq j$).

Combining the first and second laws of thermodynamics for stress-strain variables, we can define the variation of the

internal energy (dU) per unit volume of a deformed anisotropic elastic body as a function of entropy (dS) and elastic strain ($d\epsilon_{ij}$) at an absolute temperature (T) as

$$dU = \sigma_{ij} d\epsilon_{ij} + TdS$$

U and S are called state functions. From this equation, it follows that the stress tensor at constant entropy can be defined as

$$\sigma_{ij} = \left(\frac{\partial U}{\partial \epsilon_{ij}} \right) = c_{ijkl} \epsilon_{kl} \quad \text{hence} \quad c_{ijkl} = \left(\frac{\partial \sigma_{ij}}{\partial \epsilon_{kl}} \right) \quad \text{and} \quad c_{klij} = \left(\frac{\partial \sigma_{kl}}{\partial \epsilon_{ij}} \right)$$

and finally, we can write the elastic constants in terms of internal energy and strain as

$$c_{ijkl} = \frac{\partial}{\partial \epsilon_{kl}} \left(\frac{\partial U}{\partial \epsilon_{ij}} \right) = \left(\frac{\partial^2 U}{\partial \epsilon_{ij} \partial \epsilon_{kl}} \right) = \left(\frac{\partial^2 U}{\partial \epsilon_{kl} \partial \epsilon_{ij}} \right) = c_{klij}$$

The fourth-rank elastic tensors are referred to as second-order elastic constants in thermodynamics, because they are defined as second-order derivatives of a state function (e.g., internal energy $\partial^2 U$ for adiabatic or Helmholtz free energy $\partial^2 F$ for isothermal constants) with respect to strain; we obtain the Schwarz integrability condition that allows the interchanging of the order of partial derivatives of a function. It follows from these mathematical and thermodynamic arguments that the symmetry of the derivatives allows the interchange of the first pair of indexes (ij) with second (kl):

$$c_{ijkl} = c_{jikl} \quad \text{and} \quad c_{ijkl} = c_{ijlk} \quad \text{and now} \quad c_{ijkl} = c_{klij}$$

The additional symmetry of $c_{ijkl} = c_{klij}$ permutation reduces the number of independent elastic coefficients from 36 to 21, and tensor with two Voigt indexes is symmetrical, $c_{mn} = c_{nm}$. Although we have illustrated the case of isentropic (constant entropy, equivalent to an adiabatic process for a reversible process such as elasticity) elastic constants that intervene in the propagation of elastic waves whose vibration is too fast for thermal diffusion to establish heat exchange to achieve isothermal conditions, these symmetry relations are also valid for isothermal elastic constants that are used in mechanical problems. Most of the elastic constants reported in the literature are determined by the propagation of ultrasonic elastic waves and are adiabatic. More recently, elastic constants predicted by atomic modeling for mantle conditions of pressure, and in some cases temperature, are also adiabatic (see review by Karki et al., 2001, and also see Chapter 2.08).

The elastic constants in the literature are presented in the form of 6 by 6 tables for the triclinic symmetry with 21 independent values; here, the independent values are shown in bold characters in the upper diagonal of c_{mn} with the corresponding c_{ijkl} :

$$\begin{bmatrix} c_{11} & c_{12} & c_{13} & c_{14} & c_{15} & c_{16} \\ c_{12} & c_{22} & c_{23} & c_{24} & c_{25} & c_{26} \\ c_{13} & c_{23} & c_{33} & c_{34} & c_{35} & c_{36} \\ c_{14} & c_{24} & c_{34} & c_{44} & c_{45} & c_{46} \\ c_{15} & c_{25} & c_{35} & c_{45} & c_{55} & c_{56} \\ c_{16} & c_{26} & c_{36} & c_{46} & c_{56} & c_{66} \end{bmatrix} = \begin{bmatrix} c_{1111} & c_{1122} & c_{1133} & c_{1123} & c_{1113} & c_{1112} \\ c_{1122} & c_{2222} & c_{2233} & c_{2223} & c_{2213} & c_{2212} \\ c_{1133} & c_{2233} & c_{3333} & c_{3323} & c_{3313} & c_{3312} \\ c_{1123} & c_{2223} & c_{3323} & c_{2323} & c_{2313} & c_{2312} \\ c_{1113} & c_{2213} & c_{3313} & c_{2313} & c_{1313} & c_{1312} \\ c_{1112} & c_{2212} & c_{3312} & c_{2312} & c_{1312} & c_{1212} \end{bmatrix}$$

In the triclinic system, there are no special relationships between the constants. On the other extreme is the case of isotropic elastic symmetry that is defined by just two coefficients. Note that this is not the same as cubic symmetry, where there are three coefficients and that a cubic crystal can be

elastically anisotropic. The isotropic elastic constants can be expressed in the four-index system as

$$c_{ijkl} = \lambda \delta_{ij} \delta_{kl} + \mu (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk})$$

where λ is Lamé's coefficient and μ is the shear modulus. λ and μ are often referred to as Lamé's constants after the French mathematician Gabriel Lamé, who first published his book 'Leçons sur la théorie mathématique de l'élasticité des corps solides' in 1852. In the two-index Voigt system, the independent values are

$$\begin{aligned} c_{11} &= c_{22} = c_{33} = \lambda + 2\mu \\ c_{12} &= c_{23} = c_{13} = \lambda \\ c_{44} &= c_{55} = c_{66} = \frac{1}{2}(c_{11} - c_{12}) = \mu \end{aligned}$$

In matrix form, they are written as

$$\begin{bmatrix} c_{11} & c_{12} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{12} & c_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{2}(c_{11} - c_{12}) & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{2}(c_{11} - c_{12}) & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{2}(c_{11} - c_{12}) \end{bmatrix}$$

where the two independent values are c_{11} and c_{12} . Another symmetry that is very important in seismology is the transverse isotropic medium (or hexagonal crystal symmetry). In many geophysical applications of transverse isotropy, the unique symmetry direction (X_3) is vertical and the other perpendicular elastic axes (X_1 and X_2) are horizontal and share the same elastic properties and velocities. It is very common in seismological papers to use the notation of Love (1927) for the elastic constants of transverse isotropic media where

$$\begin{aligned} A &= c_{11} = c_{22} = c_{1111} = c_{2222} \\ C &= c_{33} = c_{3333} \\ F &= c_{13} = c_{23} = c_{1133} = c_{2233} \\ L &= c_{44} = c_{55} = c_{2323} = c_{1313} \\ N &= c_{66} = \frac{1}{2}(c_{11} - c_{12}) = c_{1212} = \frac{1}{2}(c_{1111} - c_{1122}) \\ \text{and } A - 2N &= c_{12} = c_{21} = c_{11} - 2c_{66} = c_{1212} = c_{2211} = c_{1111} - 2c_{1212} \end{aligned}$$

$$\begin{bmatrix} c_{11} & c_{12} & c_{13} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{12} & 0 & 0 & 0 \\ c_{13} & c_{13} & c_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{2}(c_{11} - c_{12}) \end{bmatrix} = \begin{bmatrix} A & A - 2N & F & 0 & 0 & 0 \\ A - 2N & A & F & 0 & 0 & 0 \\ F & F & C & 0 & 0 & 0 \\ 0 & 0 & 0 & L & 0 & 0 \\ 0 & 0 & 0 & 0 & L & 0 \\ 0 & 0 & 0 & 0 & 0 & N \end{bmatrix}$$

and the velocities in orthogonal directions that characterize a transverse isotropic medium are functions of the leading diagonal of the elastic tensor and are given as

$$\begin{aligned} A &= c_{11} = \rho V_{PH}^2 \quad C = c_{33} = \rho V_{PV}^2 \quad L = c_{44} = \rho V_{SH}^2 \quad N = c_{66} \\ &= \rho V_{SH}^2 \end{aligned}$$

where ρ is density, V_{PH} and V_{PV} are the velocities of horizontally (X_1 or X_2) and vertically (X_3) propagating P-waves, and V_{SH} and V_{SV} are the velocities of horizontally and vertically polarized S-waves propagating horizontally.

Elastic anisotropy can be characterized by taking ratios of the individual elastic coefficients. Thomsen (1986) introduced

three parameters to characterize the elastic anisotropy of any degree, not just weak anisotropy, for transverse isotropic medium:

$$\begin{aligned}\varepsilon &= c_{11} - c_{33}/2c_{33} = A - C/2C \\ \gamma &= c_{66} - c_{44}/2c_{44} = N - L/2L\end{aligned}$$

and

$$\begin{aligned}\delta^* &= \frac{1}{2}c_{33}^2 [2(c_{13} + c_{44})^2 - (c_{33} - c_{44})(c_{11} + c_{33} - 2c_{44})] \\ \delta^* &= \frac{1}{2}C^2 [2(F + L)^2 - (C - L)(A + C - 2L)]\end{aligned}$$

Thomsen also proposed a weak anisotropy version of the δ^* parameter:

$$\begin{aligned}\delta &= [(c_{13} + c_{44})^2 - (c_{33} - c_{44})^2/2c_{33}(c_{33} - c_{44})] \\ &= [(F + L)^2 - (C - L)^2/2C(C - L)]\end{aligned}$$

These parameters go to zero in the case of isotropy and have values of much less than one (i.e., 10%) in the case of weak anisotropy. The parameter ε describes the P-wave anisotropy and can be defined in terms of the normalized difference of the P-wave velocity in the directions parallel to the symmetry axis (X3, vertical axis) and normal to the symmetry axis (X12, horizontal plane). The parameter γ describes the S-wave anisotropy and can be defined in terms of the normalized difference of the SH wave velocity in the directions normal to the symmetry axis (X12, horizontal plane) and parallel to the symmetry axis (X3, vertical axis) but also in terms SH and SV, because SH parallel to the symmetry axis has the same velocity as SV normal to the symmetry axis:

$$\begin{aligned}\varepsilon &= Vp(X12) - Vp(X3)/Vp(X3) = V_{PH} - V_{PV}/V_{PV} \\ \gamma &= V_{SH}(X12) - V_{SH}(X3)/V_{SH}(X3) \\ &= V_{SH}(X12) - V_{SV}(X12)/V_{SV}(X12) \\ &= V_{SH} - V_{SV}/V_{SV}\end{aligned}$$

Thomsen (1986) found that the parameter δ^* controls most of the phenomena of importance for exploration geophysics, such as velocities inclined to the symmetry axis (vertical), some of which are nonnegligible even when the anisotropy is weak. The parameter δ^* is an awkward combination of elastic parameters, which is totally independent of the velocity in the direction normal to the symmetry axis (X12 horizontal plane) and which may be either positive or negative. Mensch and Rosolofosaon (1997) had extended the application of Thomsen's parameters to anisotropic media of arbitrary symmetry and the associated analysis in terms of the perturbation of a reference model that can exhibit strong S-wave anisotropy.

In the domain of one- or three-dimensional radial anisotropic seismic tomography, it has been the practice to use the parameters ϕ , ξ , and η to characterize the transverse anisotropy, where

$$\begin{aligned}\phi &= c_{33}/c_{11} = C/A = V_{PV}^2/V_{PH}^2 \\ \xi &= c_{66}/c_{44} = N/L = V_{SH}^2/V_{SV}^2 \\ \eta &= c_{13}/(c_{11} - 2c_{44}) = F/(A - 2L)\end{aligned}$$

For characterizing the anisotropy of the inner core, some authors (e.g., Song, 1997) use a variant of Thomsen's parameters, $\varepsilon'' = (c_{33} - c_{11})/2c_{11} = (C - A)/2A$ (positions of c_{11} and c_{33} reversed from Thomsen; single prime '' has been added to avoid confusion here with Thomsen's parameter), $\gamma' = (c_{66} - c_{44})/2c_{44} = (N - L)/2L$ (same as Thomsen), and $\sigma = (c_{11} + c_{33} - 4c_{44} - 2c_{13})/2c_{11} = (A + C - 4L - 2F)/2A$ (very

different from Thomsen's δ^*); others (e.g., Woodhouse et al., 1986) use

$$\begin{aligned}\alpha &= (c_{33} - c_{11})/A_0 = (C - A)/A_0 \\ \beta &= (c_{66} - c_{44})/A_0 \\ \gamma &= (c_{11} - 2c_{44} - c_{13})/A_0 = (A - 2N - F)/A_0\end{aligned}$$

where $A_0 = \rho_0 V_{p0}^2$ is calculated using the density ρ_0 and P-wave velocity V_{p0} at the center of the spherically symmetrical reference Earth model, PREM (Dziewoński and Anderson, 1981). With at least four different sets of triplets of anisotropy parameters to describe transverse isotropy in various domains of seismology, the situations are complex for a researcher who wants to compare the anisotropy from different published works. Even when comparisons are made, for example, for the inner core (Calvet et al., 2006), drawing conclusions may be difficult as the parameters reflect only certain aspects of the anisotropy.

In studying the effect of symmetry of the elastic properties of crystals, one is directly concerned with only the 11 Laue classes and not the 32 point groups, because elasticity is a centrosymmetric physical property. The velocity of an elastic wave depends on its direction of propagation in an anisotropic crystal, but not the positive or negative sense of the direction. In this chapter, we are restricting our study to second-order elastic constants, corresponding to small strains characteristic of elastic deformations associated with the propagation of seismic waves. If we wanted to consider larger finite strains or the effect of an externally applied stress, we would need to consider third-order elastic constants, as the approximation adopted in limiting the components of the strain tensor to terms of the first degree in the derivatives is no longer justified. For second-order elastic constants, the two cubic and two hexagonal Laue classes are not distinct (e.g., Brugger, 1965) and may be replaced by a single cubic and a single hexagonal class, which results in only nine distinct symmetry classes for crystals shown in Table 1.

2.20.2.2 Plane Waves and the Christoffel Equation

There two types of elastic waves, which propagate in an isotropic homogeneous elastic medium, the faster compressional (or longitudinal) wave with displacements parallel to propagation direction and slower shear (or transverse) waves with displacements perpendicular to the propagation direction. In anisotropic elastic media, there are three types, one compressional and two shear waves with in general three different velocities. In order to understand the displacements associated with different waves and their relationship to the propagation direction and elastic anisotropy, it is important to consider the equation of propagation of a mechanical disturbance in an elastic medium. If we ignore the effect of gravity, we can write the equation of displacement (u_i) as function of time (t) as

$$\rho \left(\frac{\partial^2 u_i}{\partial t^2} \right) = \left(\frac{\partial \sigma_{ij}}{\partial x_j} \right)$$

where ρ is the density and x_j is position. From Hooke's law, we can see that stress can be written as

$$\sigma_{ij} = c_{ijkl} \left(\frac{\partial u_l}{\partial x_k} \right)$$

and hence, elastodynamic equation that describes the inertial forces can be rewritten with one unknown, the displacement, as

Table 1 Second-order elastic constants of all Laue crystal symmetries

Cubic (3) 23,m,3,432, -43m, m3m	Hexagonal (5) 6,-6, 6/m, 622, 6mm, -62m, 6/mmm
$\begin{bmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{44} \end{bmatrix}$	$\begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{13} & 0 & 0 & 0 \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{2}(C_{11} - C_{12}) \end{bmatrix}$
Trigonal (6) 32,3m,-3m	
$\begin{bmatrix} C_{11} & C_{12} & C_{13} & C_{14} & 0 & 0 \\ C_{12} & C_{11} & C_{13} & -C_{14} & 0 & 0 \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ C_{14} & -C_{14} & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & C_{14} \\ 0 & 0 & 0 & 0 & C_{14} & \frac{1}{2}(C_{11} - C_{12}) \end{bmatrix}$	
Trigonal (7) 3,-3	
$\begin{bmatrix} C_{11} & C_{12} & C_{13} & C_{14} & -C_{25} & 0 \\ C_{12} & C_{11} & C_{13} & -C_{14} & C_{25} & 0 \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ C_{14} & -C_{14} & 0 & C_{44} & 0 & C_{25} \\ -C_{25} & C_{25} & 0 & 0 & C_{44} & C_{14} \\ 0 & 0 & 0 & C_{25} & C_{14} & \frac{1}{2}(C_{11} - C_{12}) \end{bmatrix}$	
Tetragonal (6) 422,4mm,-42m,4/mmm	Tetragonal (7) 4,-4,4/m
$\begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{13} & 0 & 0 & 0 \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{66} \end{bmatrix}$	$\begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & C_{16} \\ C_{12} & C_{11} & C_{13} & 0 & 0 & -C_{16} \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ C_{16} & -C_{16} & 0 & 0 & 0 & C_{66} \end{bmatrix}$
Orthorhombic (9) 222,mm2, mmm	Monoclinic (13) 2, m, 2/m
$\begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{22} & C_{23} & 0 & 0 & 0 \\ C_{13} & C_{23} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{66} \end{bmatrix}$	$\begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & C_{15} & 0 \\ C_{12} & C_{22} & C_{23} & 0 & C_{25} & 0 \\ C_{13} & C_{23} & C_{33} & 0 & C_{35} & 0 \\ 0 & 0 & 0 & C_{44} & 0 & C_{46} \\ C_{14} & C_{25} & C_{35} & 0 & C_{55} & 0 \\ 0 & 0 & 0 & C_{46} & 0 & C_{66} \end{bmatrix}$
Triclinic (21) 1,-1	
$\begin{bmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ C_{12} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ C_{13} & C_{23} & C_{33} & C_{34} & C_{35} & C_{36} \\ C_{14} & C_{24} & C_{34} & C_{44} & C_{45} & C_{46} \\ C_{15} & C_{25} & C_{35} & C_{45} & C_{55} & C_{56} \\ C_{16} & C_{26} & C_{36} & C_{46} & C_{56} & C_{66} \end{bmatrix}$	

The number in brackets is the number of independent constants.

$$\partial \left(\frac{\partial^2 u_i}{\partial t^2} \right) = c_{ijkl} \left(\frac{\partial^2 u_l}{\partial x_j \partial x_k} \right)$$

Describing the displacement of monochromatic plane wave by any harmonic form as a function of time, such as (e.g., Federov, 1968)

$$u = A \exp(i(k \cdot x - \omega t))$$

where A is the amplitude vector, which gives the direction and magnitude of particle motion; t time; n the propagation direction normal to the plane wave front; ω the angular frequency, which is related to frequency by $f = \omega/2\pi$, and k the wave vector that is related to the phase velocity (V) by $V = \omega/k$ and the plane wave front normal (n) by $k = (2\pi/\lambda) n$, where λ is the

wavelength. For plane waves, the total phase $\phi = (k \cdot x - \omega t)$ is a constant as the phase is constant along the wave front. Hence, the equation for a surface of equal phase at any instant of time (t) is a plane perpendicular to the propagation unit vector (n). If now we insert the solution for the time-dependant displacement into the elastodynamic equation, we find the Christoffel equation (Christoffel, 1877) as one of his contributions to the propagation of discontinuities as waves in elastic materials:

$$C_{ijkl} s_j s_l p_k = \rho V^2 p_i \quad \text{or} \quad C_{ijkl} s_j s_l p_k = \rho p_i$$

$$(C_{ijkl} n_j n_l - \rho V^2 \delta_{ik}) p_k = 0 \quad \text{or} \quad (C_{ijkl} s_j s_l - \rho g \delta_{ik}) p_k = 0$$

where V are the phase velocities, ρ is density, p_k are polarization unit vectors, n_j are propagation unit vectors, and s_j are the slowness vectors of magnitude $1/V$ and the same direction as the propagation direction (n). The polarization unit vectors p_k are obtained as eigenvectors and corresponding eigenvalues of the roots of the equation

$$\det \rightarrow C_{ijkl} n_j n_l - \rho V^2 \delta_{ik} \rightarrow 0 \quad \text{or} \quad \det \rightarrow C_{ijkl} s_j s_l - \rho \delta_{ik} \rightarrow 0$$

We can simplify this equation by introducing the Christoffel (Kelvin-Christoffel or acoustic) tensor $T_{ik} = C_{ijkl} n_j n_l$ and three wave moduli $M = \rho V^2$; hence, $\det \rightarrow T_{ik} - M \delta_{ik} \rightarrow 0$. The equation can be written in full as

$$\begin{vmatrix} T_{11} - M & T_{12} & T_{13} \\ T_{21} & T_{22} - M & T_{23} \\ T_{31} & T_{32} & T_{33} - M \end{vmatrix} = 0$$

which upon expansion yields the cubic polynomial in M :

$$M^3 - I_T M^2 + II_T M - III_T = 0$$

where $I_T = T_{ii}$, $II_T = \frac{1}{2} (T_{ii} T_{jj} - T_{ij} T_{ji})$, and $III_T = \det \rightarrow T_{ij} \rightarrow$ are the first, second, and third invariants of the Christoffel tensor. The three roots of the cubic polynomial in M are the three wave moduli M . The eigenvectors (e_j) associated with each wave moduli can be found by solving $(T_{ij} - M \delta_{ij}) e_j = 0$. Analytic solutions for the Christoffel tensor have been proposed in various forms by Červený (1972), Every (1980), Mainprice (1990), Mensch and Rosolofosaon (1997), and probably others.

The Christoffel tensor is symmetrical because of the symmetry of the elastic constants, and hence,

$$T_{ik} = C_{ijkl} n_j n_l = C_{jikl} n_j n_l = C_{ijlk} n_j n_l = C_{klji} n_j n_l = T_{ki}$$

The Christoffel tensor is also invariant upon the change of sign of the propagation direction (n) as the elastic tensor is not sensitive to the presence or absence of a center of symmetry, being a centrosymmetric physical property. Because the elastic strain energy ($1/2 C_{ijkl} \cdot \epsilon_{ij} \cdot \epsilon_{kl}$) of a stable crystal is always positive and real (e.g., Nye, 1957), the eigenvalues of the 3×3 Christoffel tensor (being a Hermitian matrix) are three positive real values of the wave moduli (M) corresponding to $\rho V p^2$, $\rho V s_1^2$, $\rho V s_2^2$ of the plane waves propagating in the direction n . The three eigenvectors of the Christoffel tensor are the polarization directions (also called vibration, particle movement, or displacement vectors) of the three waves; as the Christoffel tensor is symmetrical, the three eigenvectors (and polarization) vectors are mutually perpendicular. In the most general case, there are no particular angular relationships between polarization directions (p) and the propagation direction (n); however, typically, the P-wave

polarization direction is nearly parallel and the two S-wave polarizations are nearly perpendicular to the propagation direction and they are termed quasi-P- or quasi-S-waves. If the P-wave and two S-wave polarizations are, respectively, parallel and perpendicular the propagation direction, which may happen along a symmetry direction, then the waves are termed pure P and pure S or pure modes. Only velocities in pure mode directions can be directly related to single elastic constants (Neighbours and Schacher, 1967). In general, the three waves have polarizations that are perpendicular to one another and propagate in the same direction with different velocities, with $V_p > V_{s1} > V_{s2}$. A propagation direction for which two (or all three) of the phase velocities are identical is called an acoustic axis, which occurs even in crystals of triclinic symmetry. Commonly, the acoustic axis is associated with the two S-waves having the same velocity. The S-wave may be identified by their relative velocity $V_{s1} > V_{s2}$ or by their polarization being parallel to a symmetry direction or feature, for example, SH and SV, where the polarization is horizontal and vertical to the third axis of reference Cartesian frame of the elastic tensor (X3 in the terminology of Nye (1957); X3 is almost always parallel to the crystal *c*-axis) in mineral physics and perpendicular to the Earth's surface in seismology.

What is the difference between an elastic isotropic medium and an anisotropic medium for wave propagation? For an isotropic medium, the propagation direction is parallel to the V_p polarization and the V_s polarizations normal to propagation direction; all are associated with the same S velocity as $V_{s1} = V_{s2}$ and in general $V_p > V_s$. Even in isotropic medium, the S-wave polarizations are normal to P-wave polarization. What is different for anisotropic medium is that propagation direction is no longer parallel to the V_p polarization by an angle of few degrees, and the two S-wave polarizations normal to P-wave polarization are now associated different velocities ($V_{s1} > V_{s2}$). The angle between propagation direction and the V_p polarization, as well as the difference between the S-wave velocities, depends on the magnitude of the elastic anisotropy. While discussing the difference between isotropic and anisotropic media, it is pertinent to mention the case of the ratio between V_p and V_s , which is a parameter frequently measured in seismology, especially for regions where fluids may be present. It is a well-known mathematical fact that for an isotropic medium, V_p/V_s ratio can be related to Poisson's ratio (ν) by nonlinear relationship

$$\nu = \frac{1}{2} \left[\frac{(V_p/V_s)^2 - 2}{(V_p/V_s)^2 - 1} \right]$$

The mechanical Poisson's ratio is defined by the negative radial strain over the longitudinal strain $\nu = -\epsilon_r/\epsilon_l$. Clearly, Poisson's ratio does not have any physical connection with V_p/V_s , which are the velocity of a P-wave with extensional and contraction strains and that of an S-wave with shear strains even in the isotropic case; the analogy with anisotropic case is even less convincing as there are V_{s1} , V_{s2} , and V_p where the polarization strains are inclined to the propagation direction; and the mechanical situation is very far from Poisson's ratio. Hence, I strongly recommend seismologists and rock and mineral physicists to report the measurable V_p/V_{s1} and V_p/V_{s2} ratios of anisotropic media rather than Poisson's ratio derived from a calculation of dubious physical significance.

The velocity at which energy propagates in a homogenous anisotropic elastic medium is defined as the average power flow density divided by average total energy density (e.g., Auld, 1990) and can be calculated from the phase velocity using the following relationship given by Federov (1968)

$$V_i^e = C_{ijkl} p_j p_l n_k / \rho V$$

The phase and energy velocities are related by a vector equation $V_i^e \cdot n_i = V_i$. It is apparent from this relationship that V^e is not in general parallel to propagation direction (n) and has a magnitude equal or greater to the phase velocity ($V = \omega/k$). The propagation of waves in real materials occurs as packets of waves typically having a finite band of frequencies. The propagation velocity of wave packet is called the group velocity, and this is defined for plane waves of given finite-frequency range as

$$V_i^g = (\partial \omega / \partial k_i)$$

The group velocity is in general different to the phase velocity except along certain symmetry directions. In lossless anisotropic elastic media, the group and energy velocities are identical (e.g., Auld, 1990); hence, it is not necessary to evaluate the differential angular frequency versus wave vector to obtain the group velocity as $V^g = V^e$. The group velocity has direct measurable physical meaning that is not apparent for the energy or phase velocities.

Various types of plot have been used to illustrate the variation of velocity with direction in crystals. Velocities measured by the Brillouin spectroscopy are displayed using graphs of velocity as a function of propagation directions used in the experiments. The phase velocities V_p , V_{SH} , and V_{SV} of stishovite are shown in Figure 3, using the elastic constants from Weidner et al. (1982); although this type of plot may be useful for displaying the experimental results, it does not convey the

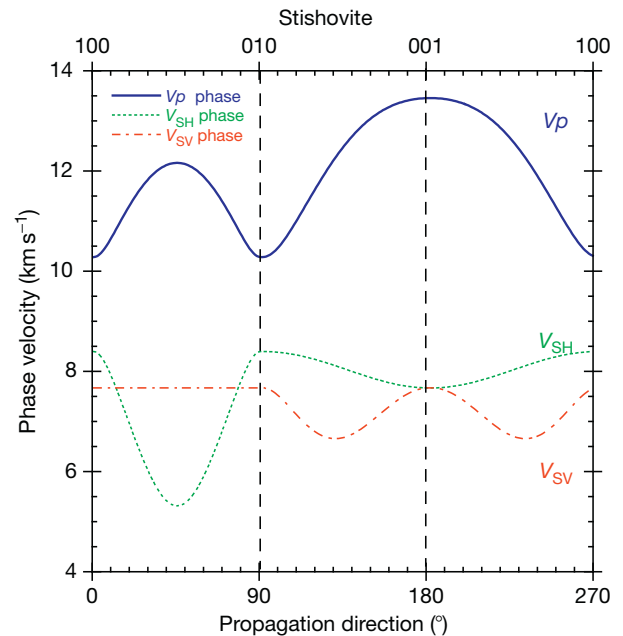


Figure 3 The variation of velocity with direction for tetragonal stishovite as described by Weidner et al. (1982).

symmetry of the crystal. In crystal acoustics, the phase velocity and slowness surfaces have traditionally illustrated the anisotropy of elastic wave velocity in crystals as a function of the propagation direction (n) and plots of the wave front (ray or group) surface given by tracing the extremity of the energy velocity vector defined earlier. The normal to the slowness surface has the special property of being parallel to the energy velocity vector. The normal to the wave front surface has the special property of being parallel to the propagation direction (n) and wave vector (k). We can illustrate these polar reciprocal properties using the elastic constants of the hcp ϵ -phase of iron, which is considered to be the major constituent of the inner core, determined by Mao et al. (1998) at high pressure (Figure 4). Notice that the twofold symmetry along the $a[2\bar{1}\bar{1}0]$ axis of hexagonal ϵ -phase is respected by the slowness and wave front surfaces of the SH waves. The wave front surface can be regarded as a recording after one second of the propagation from a spherical point source at the center of the

diagram. The wave front is a surface that separates the disturbed from the undisturbed regions. Anisotropic media have velocities that vary with direction and hence phase velocity and slowness surfaces with concave and convex undulations in three dimensions. The undulations are not sharp as velocities and slowness change slowly with orientation. In contrast, the wave surface can have sharp changes in direction, called cusps or folded wave surfaces in crystal physics (e.g., Musgrave, 2003) and triplications or caustics in seismology (e.g., Vavrycuk, 2003), particularly for S-waves, which correspond in orientation to undulations in the phase velocity and slowness surfaces. The high-pressure form of SiO_2 called stishovite illustrates the various facets of the phase velocity, slowness, and wave front surfaces in a highly anisotropic mineral (Figure 5). Velocity clearly varies strongly with propagation direction; in the case of stishovite, the variation for SH is very important, whereas SV is constant in the (001) plane. Stishovite has tetragonal symmetry, and hence, the c -axis has fourfold

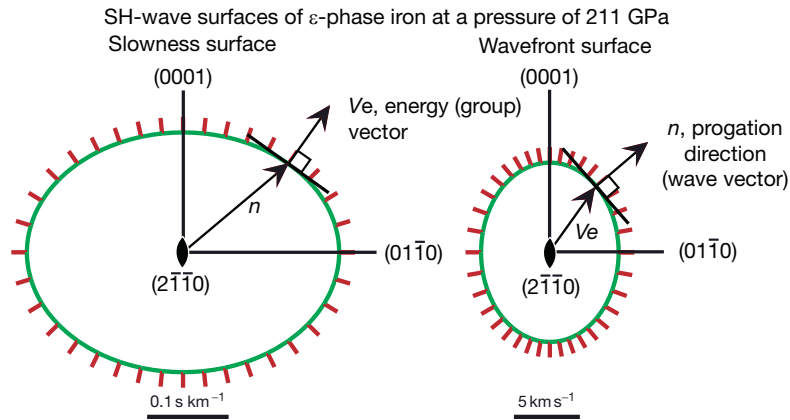


Figure 4 The polar reciprocal relation between the slowness and the wave front surfaces in hexagonal ϵ -phase iron at 211 GPa using the elastic constants determined by Mao et al. (1998). The normal to the slowness surface is the energy vector (brown), and the normal to the wave front surface is the propagation direction (parallel to the wave vector). Note the twofold symmetry on the surfaces.

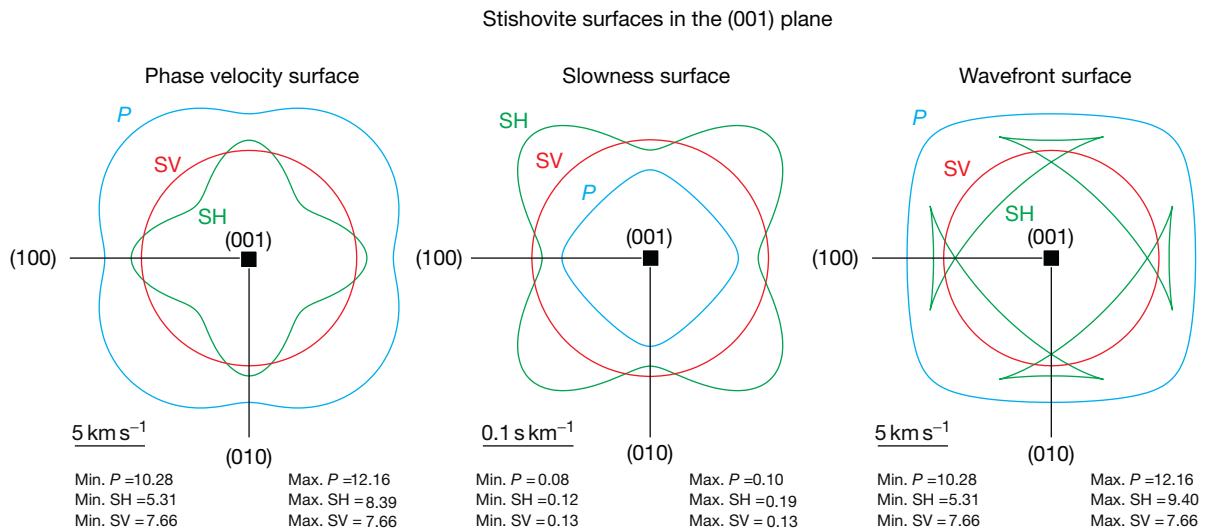


Figure 5 The three surfaces used to characterize acoustic properties, the phase velocity, and slowness and wave front surfaces for tetragonal stishovite. Note fourfold symmetry of the surfaces and the cusps on the SH wave front surface. The elastic constants of stishovite were measured by Weidner et al. (1982) at ambient conditions.

symmetry that can clearly be identified in the various surfaces in (001) plane. There are orientations where the SH and SV surfaces intersect, and hence, there is no shear wave splitting (S-wave birefringence) as both S-waves have the same velocity. The phase velocity and slowness surfaces have smooth changes in orientation corresponding to gradual changes in velocity. In contrast, along the $a[100]$ and $b[010]$ directions, the SH wave

Wavefront cusps on SH-waves in Stishovite in the (001) plane

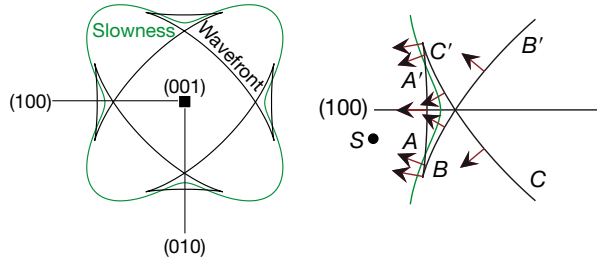


Figure 6 Cusps on the wave front surface of tetragonal stishovite and its relation to the slowness surface in the $[100]$ direction. The propagation directions of the wave front are marked by arrows every 10° . See the text for detailed discussion.

front has sharp variations in orientation called cusps. The cusps on the SH wave front are shown in more detail in **Figure 6**, where the cusps on the wave front are clearly related to minima of the slowness (or maxima on the phase velocity) surface. The propagation of SH in the $a[100]$ direction is instructive; if one considers seismometer at the point S, then seismometer will record first the arrival of wave front AA', then BB', and finally CC'. The parabolic curved nature of the cusp AA' is also at the origin of the word caustic to describe this phenomenon by analogy with the convergent rays in optics, whereas the word triplication evokes the arrival of the three wave fronts. Although we are dealing with homogeneous anisotropic medium, a single crystal of stishovite, the seismometer will record three arrivals for SH, plus of course SV and P, giving a total of five arrivals for a single mechanical disturbance. Media with tetragonal elastic symmetry are not very common in seismology, whereas media with hexagonal (or transverse isotropic) symmetry are very common and have been postulated, for example, for the D'' layer above the core-mantle boundary (CMB) (e.g., [Kendall, 2000](#)). The three surfaces of the hexagonal ϵ -phase of iron are shown in **Figure 7** in the $a(2\bar{1}\bar{1}0)$ and $c(0001)$ planes, which are, respectively, the perpendicular and parallel to the elastic symmetry axis (c -axis or X_3) of transverse isotropic elastic symmetry. I will consider

ϵ -phase iron (hexagonal) surfaces in the (100) and (001) planes

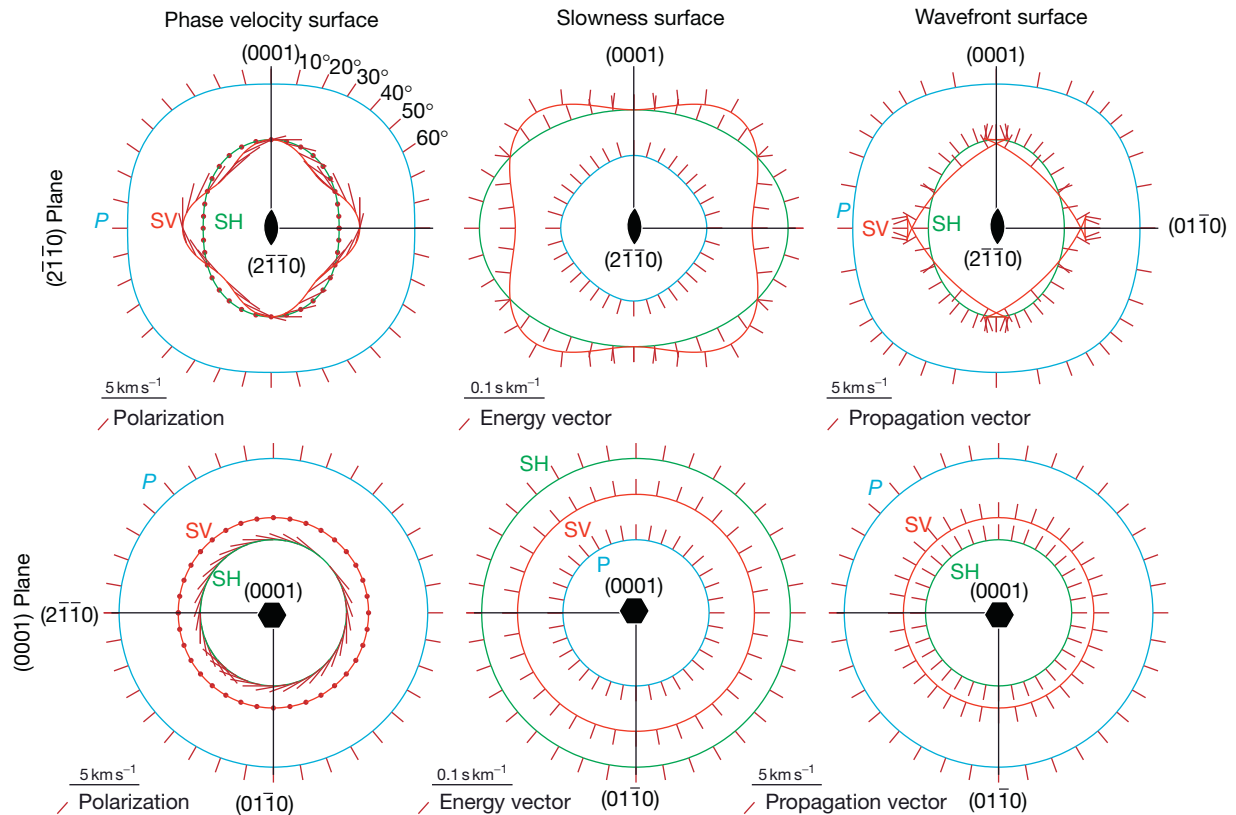


Figure 7 Velocity surfaces of ϵ -phase of iron in the second-order prism and basal plane illustrating the anisotropy in a hexagonal or transverse isotropic structure. Note the perfectly isotropic (circular) velocity surfaces in the base plane. The polarizations are marked on the phase velocity surfaces, and for the basal plane, the polarizations for P are normal to the surface and parallel to the propagation direction, whereas for S, they are normal and vertical for SV and tangential and horizontal for SH as in an isotropic medium. The energy vector and propagation direction are normal to the slowness and wave front surfaces in the basal plane.

first the wave properties in the $a(2\bar{1}\bar{1}0)$ plane. In this plane, the maximum P-wave velocity is 45° from the c -axis and minimum parallel to the a - and c -axes. The maximum SH velocity is parallel to the c -axis and the minimum parallel to b -axis, whereas the SV velocity has a maximum parallel to the a - and c -axes and a minimum 45° to the c -axis. The polarization direction of P-waves is not perpendicular to the phase velocity surface in general and not parallel to the propagation direction, except along the symmetry directions $m[01\bar{1}0]$ and $c[0001]$ axes. The SH polarizations are all normal to the c -axis, and hence, they appear as points in the $a(2\bar{1}\bar{1}0)$ plane. The SV polarizations are inclined to the a -axis, and hence, they appear as lines of variable length depending on their orientation. The SH and SV velocity surfaces intersect parallel to the c -axis and at 60° from the c -axis, where they have the same velocity. The minima in the SV slowness surface along the a - and c -axes correspond to the cusps seen on the wave front surface. The wave properties in the (0001) plane are completely different as both the P- and S-waves display a single velocity, hence the name transverse isotropy as the velocities do not vary with direction in this plane perpendicular (transverse) to the unique elastic symmetry axis (c -axis or X_3). The isotropic nature of this plane is also shown by the polarizations of the P-waves, which are normal to the phase velocity surface and parallel to the propagation direction, as in the isotropic case. Similarly for the S-waves, the polarization directions for SV are parallel and those of SH are normal to the symmetry axis, and both are perpendicular to the propagation direction.

The illustrations used so far are only two-dimensional sections of the anisotropic wave properties. Ideally, we would like to see the three-dimensional form of the velocity surfaces and polarizations. A three-dimensional plot of the P, SH, and SV velocities in Figure 8 shows the geometric relation of the polarizations to the crystallographic axes but is too complicated to see the variation in velocities; only a few directions have been plotted for clarity. A more practical representation that is directly related to spherical plot in Figure 8 is the pole figure plot of contoured and shaded velocities with polarizations shown in Figure 9. The circular nature of the velocity and polarization around the sixfold symmetry axis $c[0001]$ is immediately apparent. The maximum shear wave splitting and SV velocity are in the basal (0001) plane. From the plot, we can see that ϵ -phase of iron is very anisotropic at the experimental conditions of Mao et al. (1998) with a P-wave anisotropy of 7.1%. The shear wave anisotropy has a maximum of 26.3%, because in this transverse isotropic structure, SH has a minimum and SV has a maximum velocity in the basal plane. At first sight, the pole figure plot of polarizations appears complex. To illustrate the representation of S-wave polarizations on a pole figure, I have drawn a single propagation direction in Figure 10. I have chosen stishovite as my example mineral because it is very anisotropic, and hence, the angles between the polarizations are clearly not parallel (qP) or perpendicular ($qS1$, $qS2$) to the propagation direction.

It is important to note that for seismic and laboratory ultrasonic applications, one should use adiabatic elastic

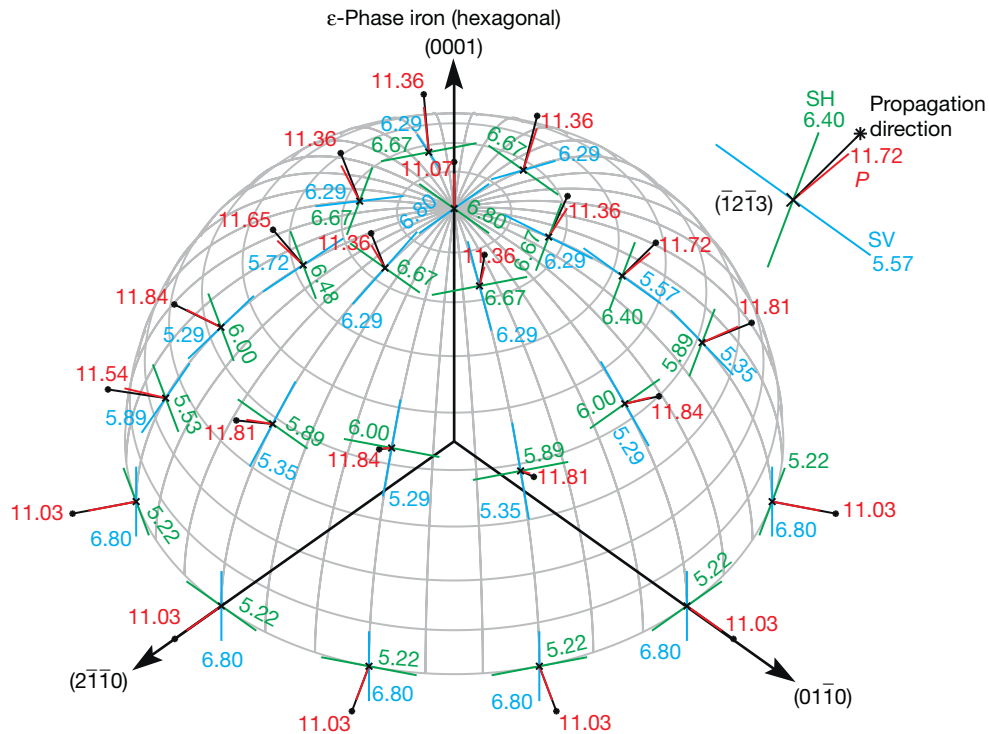
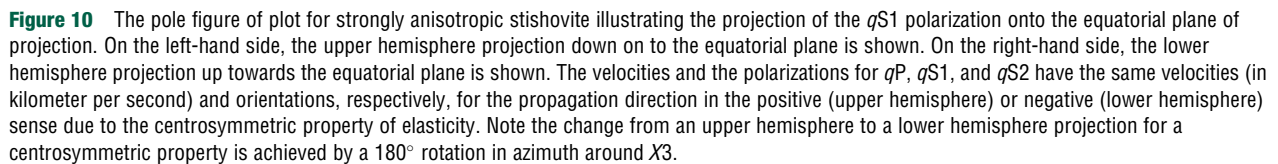
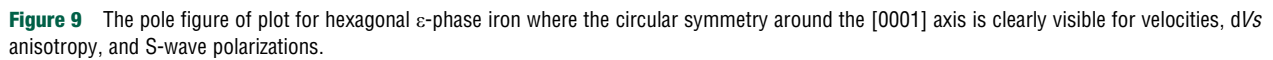


Figure 8 A 3-D illustration of the propagation direction (black), P-wave polarization (red), SH wave (green), and SV wave (blue) in hexagonal ϵ -phase iron at 211 GPa. The sphere is marked with grid at 10° intervals. The SH wave polarizations are organized around the [001] direction in a hexagonal pattern. The P-wave polarization is not in general parallel, and hence, the S-wave polarizations are not perpendicular to the propagation, as illustrated for the $[12\bar{1}3]$ direction. However, along symmetry directions, such as $[2\bar{1}\bar{1}0]$, the P-wave polarization is parallel, and hence, the S-wave polarizations are perpendicular to the propagation.



constants, as the timescale of elastic deformation is relatively short compared with timescale of thermal diffusion. Hence, thermal diffusion is too slow to obtain isothermal conditions. We can determine the correction necessary to obtain adiabatic constants from isothermal ones by considering the elastic strains caused by stresses and temperature changes:

$$d\epsilon_{ij} = \left(\frac{\partial \epsilon_{ij}}{\partial \sigma_{kl}} \right)_T d\sigma_{kl} + \left(\frac{\partial \epsilon_{ij}}{\partial T} \right)_\sigma dT$$

In this equation given by Nye (1957), the first term in brackets on the right-hand side is the elastic compliance tensor at constant temperature (T), and the second term is the thermal expansion tensor at constant entropy (σ). A second equation is required to define change in entropy due to changes in stress and temperature:

$$dS = \left(\frac{\partial S}{\partial \sigma_{kl}} \right)_T d\sigma_{kl} + \left(\frac{\partial S}{\partial T} \right)_\sigma dT$$

In this equation, the first term in brackets is the piezocaloric effect and the second term is heat capacity. If we assume that entropy is constant ($dS=0$) in the second equation and substitute the result in the first equation, we can eliminate dT and we obtain

$$d\epsilon_{ij} = \left(\frac{\partial \epsilon_{ij}}{\partial \sigma_{kl}} \right)_T d\sigma_{kl} - \left(\frac{\partial \epsilon_{ij}}{\partial T} \right)_\sigma \left(\frac{\partial S}{\partial \sigma_{kl}} \right)_T d\sigma_{kl} / \left(\frac{\partial S}{\partial T} \right)_\sigma$$

Dividing the resulting equation by $d\sigma_{kl}$ and using the relation

$$\left(\frac{\partial \epsilon_{ij}}{\partial T} \right)_\sigma = \left(\frac{\partial S}{\partial \sigma_{kl}} \right)_T$$

gives the final result

$$\begin{aligned} \left(\frac{\partial \epsilon_{ij}}{\partial \sigma_{kl}} \right)_S - \left(\frac{\partial \epsilon_{ij}}{\partial \sigma_{kl}} \right)_T &= - \left(\frac{\partial S}{\partial \sigma_{kl}} \right)_\sigma \left(\frac{\partial \epsilon_{ij}}{\partial T} \right)_\sigma \left(\frac{\partial T}{\partial S} \right)_\sigma \\ &= \left(\frac{\partial \epsilon_{ij}}{\partial T} \right)_\sigma \left(\frac{\partial \epsilon_{kl}}{\partial T} \right)_\sigma \left(\frac{\partial T}{\partial S} \right)_\sigma \end{aligned}$$

In tensor notation, this is the equation for the difference between adiabatic and isothermal compliance tensors:

$$\begin{aligned} S_{ijkl}^S - S_{ijkl}^T &= -\alpha_{ij}\alpha_{kl}(T/C_v) = -\alpha_{ij}\alpha_{kl}(T/\rho C_p) \\ S_{ijkl}^S &= S_{ijkl}^T - \alpha_{ij}\alpha_{kl}(T/\rho C_p) \end{aligned}$$

where the tensor superscript S stands for adiabatic and T for isothermal, α_{ij} is thermal expansion tensor, T is absolute temperature in Kelvin, C_v is heat capacity per unit volume at constant strain, C_p is specific heat capacity at constant pressure, and ρ is density. In a similar way, we can derive the result for stiffness tensors as

$$C_{ijkl}^S = C_{ijkl}^T + \lambda_{ij}\lambda_{kl}(T/\rho C_v)\lambda = \alpha_{ij}\alpha_{kl}C_{ijkl}^T$$

where C_v is specific heat capacity at constant volume. The adiabatic stiffness tensor will have greater values than isothermal stiffness tensor in general. Stiffness tensors determined by *ab initio* modeling in static conditions ($T=0$ K) are a special case as there is no difference between adiabatic and isothermal tensors. At ambient temperature ($T=300$ K), the difference between adiabatic and isothermal tensors is typically less than 1%, whereas at 3500 K and 48 GPa, it increases to 7%

for Mg-perovskite (Zhang et al., 2013) and is 13% at 6000 K and 360 GPa for hcp iron in the inner core (Steinle-Neumann et al., 2001). For the discussion of the effect of pressure on these tensors, see Chapter 2.08.

2.20.2.3 Measurement of Elastic Constants

Elastic properties can be measured by a various methods, including mechanical stress-strain, ultrasonic, Brillouin spectroscopy, nonhydrostatic radial x-ray diffraction (RXD), x-ray and neutron inelastic scattering, and shock measurements. In addition to physical measurements, atomic-scale first-principles methods can predict elastic properties of crystals (see review by Karki et al., 2001; also see Chapter 2.08). The classical mechanical stress-strain measurements of elastic constants are no longer used due to the large errors, and most compilations of single-crystal elastic constants (e.g., Anderson and Isaak, 1995; Bass, 1995; Isaak, 2001) are mainly based on ultrasonic measurements, the traditional technique at ambient conditions for large specimens. The measurement of the elastic constants for minerals from the deep Earth using classical techniques requires large (~ 1 cm³) gem quality crystals. However, many minerals of the deep Earth are not stable, or metastable, at ambient conditions and no large gem quality crystals are available. Furthermore, the main applications of elastic constants are for the interpretation of seismological data at the high-pressure and high-temperature conditions of the Earth's mantle and core. Although ultrasonic techniques are still widely used, new methods are constantly being developed and refined for measurements at higher pressures and temperatures (Jacobsen et al., 2005; Li et al., 2004; Liebermann and Li, 1998).

Ultrasonic measurements require a mechanical contact between the transducers that produce and detect the ultrasonic signal and the sample. For experiments at high pressure and temperature, the contact is generally made via the high-pressure pistons and a high-temperature ceramic buffer rod or directly with the diamond anvils. Various corrections are necessary to take into account the ray paths through the pistons and buffer rods and transducer-bond phase shift effects. The technique most commonly used is based on the ultrasonic interferometry method introduced by Jackson and Niesler (1982) to obtain accurate pressure derivatives of single-crystal MgO to 3 GPa in a piston cylinder apparatus. The use of ultrasonic interferometry in conjunction with synchrotron x-radiation in multianvil devices permits a more accurate measurement of elastic constants at simultaneous high pressure and temperature (Li et al., 2004), as the sample length can be directly measured by x-radiography *in situ*, thereby reducing uncertainties in velocity measurements. A new gigahertz ultrasonic interferometer has been recently developed for the diamond anvil cell (DAC; Jacobsen et al., 2005). The gigahertz frequency reduces the wavelength in minerals to a few micrometers, which allows the determination of velocity and the elastic constants for samples of a few tens of micrometers in thickness. Another ultrasonic technique called resonant ultrasound spectroscopy has been used to study the elastic constants of minerals with high precision to very high temperatures at ambient pressure (e.g., Isaak, 1992; Isaak et al., 2005).

Brillouin scattering spectroscopy has become an established tool for measuring elastic constants since the introduction of laser sources and multipass Fabry–Perot interferometers (e.g., Vacher and Boyer, 1972). Unlike the ultrasonic techniques that usually measure the velocity in relatively few crystallographic directions, and where possible in pure mode directions, using Brillouin scattering, the velocities can be measured along many propagation directions and the numerous velocities are inverted to obtain a least-squares determination of the elastic constants (Weidner and Carleton, 1977), and hence, it is very suitable for the measurement of low-symmetry crystals. Brillouin scattering has several advantages for measurements of transparent minerals at high pressure and temperature in a DAC, it only requires a small sample, no physical contact with the sample is required, and the Brillouin peaks increase with temperature (Sinogeikin et al., 2005). The elastic constants of MgO have been determined to high pressure (55 GPa, Zha et al., 2000) and high temperature (1500 K, Sinogeikin et al., 2005) using Brillouin scattering. A related technique using laser-induced phonon spectroscopy in the form of impulsive scattering in a DAC has been used to measure elastic constants of mantle minerals to 20 GPa (e.g., Abramson et al., 1977; Chai et al., 1977a,b).

Several x-ray and neutron diffraction and scattering techniques (e.g., Fiquet et al., 2004) have recently been developed to explore elastic behavior at extreme pressures (>100 GPa) in diamond anvils. Experiments using radial RXD of polycrystalline samples under nonhydrostatic stress have been used to estimate the single-crystal elastic constants by using the measured lattice strains and CPO combined with model polycrystalline stress distribution (e.g., Reuss uniform stress field) (e.g., Mao et al., 1998, 2008a,b,c; Merkel et al., 2005, 2006b). The uncertainties in the absolute value of the elastic constants may be on the order of 10–20%, and model-dependent stress or strain distributions may be limited by the presence of elastic and plastic strain in some cases; however, this technique provides valuable information at extreme pressures. Inelastic x-ray scattering (IXS) has provided volume-averaged P-wave velocities of hcp iron as a function of pressures to 112 GPa and temperatures up to 1100 K (Antonangeli et al., 2004, 2010, 2012; Fiquet et al., 2001). Using knowledge of the CPO combined with different scattering geometries, Antonangeli et al. (2004) had determined the P-wave velocities in two directions and C_{11} elastic constant of hcp iron. The nuclear-resonant IXS technique provides a direct probe of the phonon density of states. By the integration of the measured phonon density of states, the elastic and thermodynamic parameters are obtained, and when combined with a thermal equation of state (EOS), the P- and S-wave velocities of hcp iron have been determined to 73 GPa and 1700 K in a laser-heated DAC by Lin et al. (2005). However, it has only recently been realized that RXD and IXS elastic constant or velocity determinations can be compromised by nonhydrostatic stresses in DACs and the elastic lattice strain equation is violated by the presence of plastic strain caused by differential stresses above the plastic yield stress of the crystals in some cases (Antonangeli et al., 2006; Mao et al., 2008a,b,c; Merkel et al., 2006b, 2009).

2.20.2.4 Effective Elastic Constants for Crystalline Aggregates

The calculation of the physical properties from microstructural information (crystal orientation, volume fraction, grain shape,

etc.) is important for upper mantle rocks because it gives insight into the role of microstructure in determining the bulk properties and it is also important for synthetic aggregates experimentally deformed at simulated conditions of the Earth's interior. A calculation can be made for the *in situ* state at high temperature and pressure of the deep Earth for samples where the microstructure has been changed by subsequent chemical alteration (e.g., the transformation from olivine to serpentine) or mechanically induced changes (e.g., fractures created by decompression). The *in situ* temperatures and pressures can be simulated using the appropriate single-crystal derivatives. Additional features not necessarily preserved in the recovered microstructure, such as the presence of fluids (e.g., magma), can be modeled (e.g., Blackman and Kendall, 1997; Mainprice, 1997; Williams and Garnero, 1996). Finally, the effect of phase change on the physical properties can also be modeled using these methods (e.g., Mainprice et al., 1990). Modeling is essential for anisotropic properties as experimental measurements in many directions necessary to fully characterize anisotropy are not currently feasible for the majority of the temperature and pressure conditions found in the deep Earth.

In the following, we will only discuss the elastic properties needed for seismic velocities, but the methods apply to all tensorial properties where the bulk property is governed by the volume fraction of the constituent minerals. Many properties of geophysical interest are of this type, for example, thermal conductivity, thermal expansion, elasticity, and seismic velocities. However, these methods do not apply to properties determined by the connectivity of a phase, such as the electrical conductivity of rocks with conductive films on the grain boundaries (e.g., carbon). We will assume the sample may be microscopically heterogeneous due to grain size, shape, orientation, or phase distribution but will be considered macroscopically uniform. The complete structural details of the sample are in general never known, but a 'statistically uniform' sample contains many regions, which are compositionally and structurally similar, each fairly representative of the entire sample. The local stress and strain fields at every point $\mathbf{r}$ in a linear elastic polycrystal are completely determined by Hooke's law as follows:

$$\sigma_{ij}(\mathbf{r}) = C_{ijkl}(\mathbf{r}) \varepsilon_{kl}(\mathbf{r})$$

where $\sigma_{ij}(\mathbf{r})$ is the stress tensor, $C_{ijkl}(\mathbf{r})$ is the elastic stiffness tensor, and $\varepsilon_{kl}(\mathbf{r})$ is the strain tensor at point $\mathbf{r}$. The evaluation of the effective constants of a polycrystal would be the summation of all components as a function of position, if we know the spatial functions of stress and strain. The average stress $\langle \sigma \rangle$ and strain $\langle \varepsilon \rangle$ of a statistically uniform sample are linked by an effective macroscopic modulus C^* that obeys Hooke's law of linear elasticity:

$$C^* = \langle \sigma \rangle \langle \varepsilon \rangle^{-1}$$

where $\langle \varepsilon \rangle = \frac{1}{V} \int \varepsilon(\mathbf{r}) d\mathbf{r}$ and $\langle \sigma \rangle = \frac{1}{V} \int \sigma(\mathbf{r}) d\mathbf{r}$ where V is the volume and the notation $\langle \rangle$ denotes an ensemble average. The stress $\sigma(\mathbf{r})$ and strain $\varepsilon(\mathbf{r})$ distribution in a real polycrystal varies discontinuously at the surface of grains. By replacing the real polycrystal with a 'statistically uniform' sample, we are assuming that $\sigma(\mathbf{r})$ and strain $\varepsilon(\mathbf{r})$ are varying slowly and continuously with position $\mathbf{r}$.

A number of methods are available for determining the effective macroscopic effective modulus of an aggregate.

We will briefly present these methods, which try to take into account an increasing amount of microstructural information, which of course results in increasing theoretical complexity but yields estimates, which are closer to experimental values. The methods can be classified by using the concept of the order of the statistical probability functions used to quantitatively describe the microstructure (Kröner, 1978). A zero-order bound is given when one has no statistical information of the microstructure of the polycrystal and, for example, we do not know the orientation of the component crystals, and in this case, we have to use the single-crystal properties. The maximum and minimum of the single-crystal property are the zero-order bounds. The simplest and best-known averaging techniques for obtaining estimates of the effective elastic constants of polycrystals are the Voigt (1928) and Reuss (1929) averages. These averages only use the volume fraction of each phase, the orientation, and the elastic constants of the single crystals or grains. In terms of statistical probability functions, these are first-order bounds as only the first-order correlation function is used, which is the volume fraction. Note that no information about the shape or position of neighboring grains is used. The Voigt average is found by simply assuming that the strain field is everywhere constant (i.e., $\varepsilon(\mathbf{r})$ is independent of $\mathbf{r}$). The strain at every position is set equal to the macroscopic strain of the sample. C^* is then estimated by a volume average of local stiffnesses $C(\mathbf{g}_i)$ with orientation $\mathbf{g}_i$ and volume fraction V_i :

$$C^* \approx C_{\text{Voigt}} = \left[\sum_i V_i C(\mathbf{g}_i) \right]$$

Reuss average is found by assuming that the stress field is everywhere constant. The stress at every position is set equal to the macroscopic stress of the sample. C^* or S^* is then estimated by the volume average of local compliances $S(\mathbf{g}_i)$:

$$C^* \approx C^{\text{Reuss}} = \left[\sum_i V_i S(\mathbf{g}_i) \right]^{-1}$$

$$S^* \approx S^{\text{Reuss}} = \left[\sum_i V_i S(\mathbf{g}_i) \right]$$

$$C^{\text{Voigt}} \neq C^{\text{Reuss}} \quad \text{and} \quad C^{\text{Voigt}} \neq [S^{\text{Reuss}}]^{-1}$$

These two estimates are not equal for anisotropic solids with the Voigt being an upper bound and the Reuss a lower bound. A physical estimate of the moduli should lie between the Voigt and the Reuss average bounds as the stress and strain distributions are expected to be somewhere between uniform strain (the Voigt bound) and uniform stress (the Reuss bound). Hill (1952) observed that arithmetic mean (and the geometric mean) of the Voigt and Reuss bounds, sometimes called the Hill or Voigt–Reuss–Hill (VRH) average, is often close to experimental values. The VRH average has no theoretical justification. As it is much easier to calculate the arithmetic mean of the Voigt and Reuss elastic tensors, all authors have tended to apply the Hill average as an arithmetic mean. In Earth sciences, the Voigt, Reuss, and Hill averages have been widely used for averages of oriented polyphase rocks (e.g., Crosson and Lin, 1971). Although the Voigt and Reuss bounds are often far apart for anisotropic materials, they still provide the limits within which the experimental data should be found.

Several authors have searched for a geometric mean of oriented polycrystals using the exponent of the average of the natural logarithm of the eigenvalues of the stiffness matrix (Matthies and Humbert, 1993). Their choice of this averaging procedure was guided by the fact that the ensemble average

elastic stiffness $\langle C \rangle$ should equal the inverse of the ensemble average elastic compliances $\langle S \rangle - 1$, which is not true, for example, of the Voigt and Reuss estimates. A method of determining the geometric mean for arbitrary orientation distributions has been developed (Matthies and Humbert, 1993). The method derives from the fact that a stable elastic solid must have an elastic strain energy that is positive. It follows from this that the eigenvalues of the elastic matrix must all be positive. Comparison between the Voigt, Reuss, and Hill and the self-consistent estimates shows that the geometric mean provides estimates very close to the self-consistent method but at considerably reduced computational complexity (Matthies and Humbert, 1993). The condition that the macroscopic polycrystal elastic stiffness $\langle C \rangle$ must equal the inverse of the aggregate elastic compliance $\langle S \rangle - 1$ would appear to be a powerful physical constraint on the averaging method (Matthies and Humbert, 1993). However, the arithmetic (Hill) and geometric means are very similar (Mainprice and Humbert, 1994), which tends to suggest that they are just mean estimates with no additional physical significance.

The second set of methods uses additional information on the microstructure to take into account the mechanical interaction between the elastic elements of the microstructure. Mechanical interaction will be very important for rocks containing components of very different elastic moduli, such as solids, liquids, gases, and voids. The most important approach in this area is the ‘self-consistent’ (SC) method (e.g., Hill, 1965). The SC method was introduced for materials with a high concentration of inclusions where the interaction between inclusions is significant. In the SC method, an initial estimate of the anisotropic homogeneous background medium of the polycrystal is calculated using the traditional volume-averaging method (e.g., Voigt). All the elastic elements (e.g., grains and voids) are inserted into the background medium using Eshelby’s (1957) solution for a single ellipsoidal inclusion in an infinite matrix. The elastic moduli of the ensemble, inclusion, and background medium are used as the ‘new’ background medium for the next inclusion. The procedure is repeated for all inclusions and repeated in an iterative manner for the polycrystal until a convergent solution is found. The interaction is notionally taken into account by the evolution of the background medium that contains information about the inclusions, albeit in a homogenous form. As the inclusion can have an ellipsoidal shape, an additional microstructural parameter is taken into account by this type of model. A hybrid self-consistent method that combines elements of the geometric mean for the calculation of the elastic properties of multiphase rock samples has been introduced by Matthies (2010, 2012).

Several people (e.g., Bruner, 1976) have remarked that the SC progressively overestimates the interaction with increasing concentration. They proposed an alternative differential effective medium (DEM) method in which the inclusion concentration is increased in small steps with a reevaluation of the elastic constants of the aggregate at each increment. This scheme allows the potential energy of the medium to vary slowly with inclusion concentration (Bruner, 1976). Since the addition of inclusions to the background material is made in very small increments, one can consider the concentration step to be very dilute with respect to the current effective medium. It follows that the effective interaction between inclusions can be considered negligible and we can use the

inclusion theory of Eshelby (1957) to take into account the interaction. In contrast, the SC uses Eshelby's theory plus an iterative evaluation of the background medium to take into account the interaction. Mainprice (1997) had compared the results of SC and DEM for anisotropic oceanic crustal and mantle rocks containing melt inclusions and found the results to be very similar for melt fractions of less than 30%. At higher melt fractions, the SC exhibits a threshold value around 60% melt, whereas the DEM varies smoothly up a 100% melt. The presence of a threshold in the SC calculations is due to the specific way that the interaction is taken into account. The estimates of both methods are likely to give relatively poor results at high fractions of a phase with strong elastic contrast with the other constituents as other phenomena, such as mechanical localization related to the percolation threshold, are likely to occur.

The third set of methods uses higher-order statistical correlation functions to take into account the first- or higher-order neighbor relations of the various microstructural elements. The factors that need to be statistically described are the elastic constants (determined by composition), orientation, and relative position of an element. If the element is considered to be small relative to grain size, then grain shape and the heterogeneity can be accounted for the relative position correlation function. Nearest neighbors can be taken into account using two-point correlation function, which is also called an autocorrelation function by some authors. If we use the 'statistically uniform' sample introduced earlier, we are effectively assuming that all the correlation functions used to describe the microstructure up to order infinity are statistically isotropic; this is clearly a very strong assumption. In the special case where all the correlation functions up to order infinity are defined, Kröner (1978) had shown that the upper and lower bounds converge for the self-consistent method so that $C_{sc} = (S_{sc}) - 1$. The statistical continuum approach is the most complete description and has been extensively used for model calculations (e.g., Beran et al., 1996; Mason and Adams, 1999). Until recently, it has been considered too involved for practical application. With the advent of automated determination of crystal orientation and positional mapping using electron backscattered diffraction (EBSD) in the scanning electron microscope (Adams et al., 1993), digital microstructural maps are now available for the determination of statistical correlation functions. This approach provides the best possible estimate of the elastic properties but at the expense of considerably increased computational complexity.

The fact that there is a wide separation in the Voigt and Reuss bounds for anisotropic materials is caused by the fact that the microstructure is not fully described by such methods. However, despite the fact that these methods do not take into account such basic information as the position or the shape of the grains, several studies have shown that the Voigt average or the Hill average is within 5–10% of experimental values for low-porosity rocks free of fluids. For example, Barruol and Kern (1996) showed for several anisotropic lower crust and upper mantle rocks from the Ivrea zone in Italy that the Voigt average is within 5% of the experimentally measured velocity. Finally, from a practical point of view, a free and open-source MTEX toolbox is now available (<https://code.google.com/p/mtex/>) for effective medium calculations, such as Voigt, Reuss, and

Hill averages for second-, third-, and fourth-rank tensors, and plotting the results, a wide variety of graphic formats. A detailed description of the application of MTEX to elastic and seismic properties can be found in Mainprice et al. (2011).

2.20.2.5 Seismic Properties of Polycrystalline Aggregates at High Pressure and Temperature

The orientation of crystals in a polycrystal can be measured by volume diffraction techniques (e.g., x-ray or neutron diffraction) or individual orientation measurements (e.g., U-stage and optical microscope, electron channeling, or EBSD). In addition, numerical simulations of polycrystalline plasticity also produce populations of crystal orientations at mantle conditions (e.g., Tommasi et al., 2004). An orientation, often given the letter $\mathbf{g}$, of a grain or crystal in sample coordinates can be described by the rotation matrix between crystal and sample coordinates. In practice, it is convenient to describe the rotation by a triplet of Euler angles, for example, $\mathbf{g} = (\varphi_1 \phi \varphi_2)$ used by Bunge (1982). One should be aware that there are many different definitions of Euler angles that are used in the physical sciences. The orientation distribution function (ODF) $f(\mathbf{g})$ is defined as the volume fraction of orientations with an orientation in the interval between $\mathbf{g}$ and $\mathbf{g} + d\mathbf{g}$ in a space containing all possible orientations given by

$$\Delta V/V = \int f(\mathbf{g}) d\mathbf{g}$$

where $\Delta V/V$ is the volume fraction of crystals with orientation $\mathbf{g}$, $f(\mathbf{g})$ is the texture function, and $d\mathbf{g} = 1/8\pi^2 \sin \phi d\varphi_1 d\phi d\varphi_2$ is the volume of the region of integration in orientation space.

To calculate the seismic properties of a polycrystal, one must evaluate the elastic properties of the aggregate. In the case of an aggregate with a crystallographic fabric, the anisotropy of the elastic properties of the single crystal must be taken into account. For each orientation $\mathbf{g}$, the single-crystal properties have to be rotated into the specimen coordinate frame using the orientation or rotation matrix g_{ij} :

$$C_{ijkl}(\mathbf{g}) = g_{ip} g_{jq} g_{kr} g_{lt} C_{pqrt}(\mathbf{g}_o)$$

where $C_{ijkl}(\mathbf{g})$ is the elastic property in sample coordinates, $g_{ij} = g(\varphi_1 \phi \varphi_2)$ is the measured orientation in sample coordinates, and $C_{pqrt}(\mathbf{g}_o)$ is the elastic property in crystal coordinates.

The elastic properties of the polycrystal may be calculated by integration over all possible orientations of the ODF. Bunge (1982) had shown that integration is given as

$$\langle C_{ijkl} \rangle_m = \int C_{ijkl} m(\mathbf{g}) f(\mathbf{g}) d\mathbf{g}$$

where $\langle C_{ijkl} \rangle_m$ is the elastic properties of the aggregate of mineral m . Alternatively, it may be determined by simple summation of individual orientation measurements:

$$\langle C_{ijkl} \rangle_m = \sum C_{ijkl} m(\mathbf{g}) \cdot v(\mathbf{g})$$

where $v(\mathbf{g})$ is the volume fraction of the grain in orientation $\mathbf{g}$. For example, the Voigt average of the rock for m mineral phases of volume fraction $v(m)$ is given as

$$\langle C_{ijkl} \rangle_{\text{Voigt}} = \sum v(m) \langle C_{ijkl} \rangle_m$$

The final step is the calculation of the three seismic phase velocities by the solution of the Christoffel equation, details of which are given earlier.

To calculate the elastic constants at pressures and temperatures, the single-crystal elastic constants are given at the pressure and temperature of their measurement by using the following relationship:

$$C_{ij}(PT) = C_{ij}(P_o T_o) + (dC_{ij}/dP)\Delta P + 1/2(d^2C_{ij}/dP^2)\Delta P^2 + (dC_{ij}/dT)\Delta T + (d^2C_{ij}/dPdT)\Delta P\Delta T$$

where $C_{ij}(PT)$ are the elastic constants at pressure P and temperature T , $C_{ij}(P_o T_o)$ are the elastic constants at a reference pressure P_o (e.g., 0.1 MPa) and temperature T_o (e.g., 25 °C), dC_{ij}/dP is the first-order pressure derivative, dC_{ij}/dT is the first-order temperature derivative, $\Delta P = P - P_o$, and $\Delta T = T - T_o$. The equation is a Maclaurin expansion of the elastic tensor as a function of pressure and temperature, which is a special case of a Taylor expansion as the series is developed about the elastic constants at the reference condition $C_{ij}(P_o T_o)$. The series only represent the variation of the C_{ij} in their intervals of pressure and temperature of convergence, in other words the pressure and temperature range of the experiments or atomic modeling calculations used to determine the derivatives. Note that this equation is not a polynomial and care has to be taken when using the results of data fitted to polynomials, as, for example, the second-order derivatives fitted to a polynomial should be multiplied by two for use in the equation mentioned earlier, for example, second-order pressure derivatives for MgO given by Sinogeikin et al., (2001). Also note that this equation is not a Eulerian finite strain EOS (e.g., Davies, 1974; see succeeding text), and data fit to such an equation will not have derivatives compatible with the equation mentioned earlier, for example, the pressure derivatives of brucite determined by Jiang et al. (2006). The second-order pressure derivatives d^2C_{ij}/dP^2 are available for an increasing number of mantle minerals (e.g., olivine, orthopyroxene, garnet, and MgO), and the first-order temperature derivatives seem to adequately describe the temperature dependence of most minerals, although the second-order derivatives are also available in a few cases (e.g., garnet, fayalite, forsterite, and rutile; see Isaak, 2001 for references). Experimental measurements of the cross pressure-temperature derivatives $d^2C_{ij}/dPdT$ (i.e., the temperature derivative of the C_{ij}/dP at constant temperature) are still very rare. For example, despite the fact that MgO (periclase) is a well-studied reference material for high-pressure studies, the complete set of single-crystal cross derivatives were measured for the first time by Chen et al. (1998) to 8 GPa and 1600 K. The effect of the cross derivatives on the V_p and dV_s anisotropy of MgO is dramatic, and the anisotropy is increased by a factor of 2 when cross derivatives are used (Figure 11). Note that when a phase transition occurs, then the specific changes in elastic constants at pressures near the phase transition will have to be taken into account, for example, the SiO_2 polymorphs (Carpenter, 2006; Cordier et al., 2004a; Karki et al., 1997c). The seismic velocities also depend on the density of the minerals at pressure and temperature, which can be calculated using an appropriate EOS (Knittle, 1995). The Murnaghan EOS derived from finite strain is sufficiently accurate at

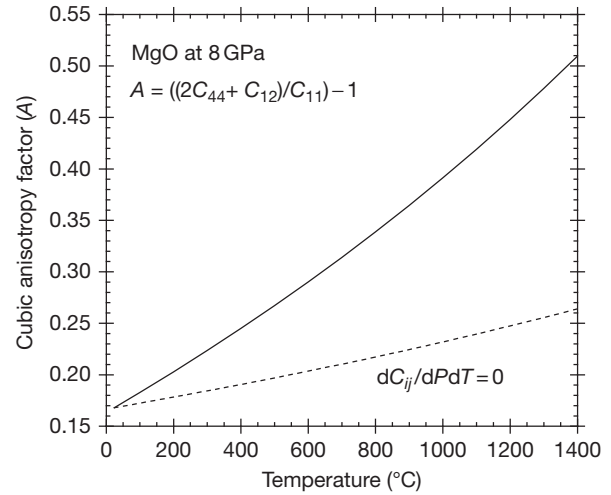


Figure 11 An illustration of the importance of the cross pressure-temperature derivatives for cubic MgO at 8 GPa pressure. With increasing temperature at constant pressure, the anisotropy measured by the cubic anisotropy factor (A) increases by a factor of 2. Data from Chen et al. (1998).

moderate compressions (Knittle, 1995) of the upper mantle and leads to the following expression for density as a function of pressure:

$$\rho(P) = \rho_o (1 + (K'/K) \cdot (P - P_o))^{1/K'}$$

where K is the bulk modulus, $K' = dK/dP$ is the pressure derivative of K , and ρ_o is the density at reference pressure P_o and temperature T_o . For temperature, the density varies as

$$\rho(T) = \rho_o \left[1 - \int \alpha_v(T) dT \right] \approx \rho_o [1 - \alpha_{av}(T - T_o)]$$

where $\alpha_v(T) = 1/V(\partial V/\partial T)$ is the volume thermal expansion coefficient as a function of temperature and α_{av} is an average value of thermal expansion that is constant over the temperature range (Fei, 1995). According to Watt (1988), an error of less than 0.4% on the P and S velocity results from using α_{av} to 1100 K for MgO. For temperatures and pressures of the mantle, the density is described for this chapter by

$$\rho(P, T) = \rho_o \left\{ (1 + (K'/K) \cdot (P - P_o))^{1/K'} [1 - \alpha_{av}(T - T_o)] \right\}$$

An alternative approach for the extrapolation elastic constants to very high pressures is Eulerian finite strain theory (e.g., Davies, 1974). The theory is based on a Maclaurin expansion of the free energy in terms of Eulerian finite volumetric strain. For example, Karki et al. (2001) reformulated Davies's equations for the elastic constants in terms of finite volumetric strain (f) as

$$C_{ijkl}(f) = (1 + 2f)^{7/2} [C_{oijkl} + b_1 f + 1/2 b_2 f^2 + \dots] - P \Delta_{ijkl}$$

where

$$\begin{aligned} f &= 1/2 [(V_o/V)^{2/3} - 1] \\ b_1 &= 3K_o (dC_{oijkl}/dP) - 5C_{oijkl} \\ b_2 &= 9K_o^2 (d^2C_{oijkl}/dP^2) + 3(K_o/dP) (b_1 + 7C_{oijkl}) \\ &\quad - 16b_1 - 49C_{oijkl} \\ \Delta_{ijkl} &= -\delta_{ij}\delta_{kl} - \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk} \end{aligned}$$

This formulation in terms of finite strain can be very useful for finding the elastic constants at a given pressure from series of *ab initio* calculations at different pressures, for example, room pressure. With the advent of practical computational methods for applying first-principles (*ab initio*) methods to calculation of elastic constants of minerals at extreme pressures reduces the Eulerian finite strain theory to a descriptive tool, if tensors are available at the appropriate pressure (and temperature) conditions. The simple Maclaurin series expansions given earlier for pressure and temperature are a compact way of describing the variation of the elastic tensors in experiments at high pressure and temperature. Extrapolation of the simple Maclaurin series expansions outside the range of experimental (or computational) data is not recommended, as the formulation is descriptive. The Eulerian finite volumetric strain formulation has the merit of a physical basis, and hence, extrapolation beyond the experimental data range may be undertaken with caution. In practice, applications of the Eulerian finite volumetric strain formulation have been mainly limited to high-symmetry crystals (e.g., Li et al., 2006b, cubic Ca-perovskite, trigonal brucite Jiang et al., 2006) but can be applied to lower symmetries (e.g., monoclinic chlorite Mookherjee and Mainprice, 2014). A thermodynamically correct formulation of the problem intermediate values in terms of pressure and temperature has been proposed by Stixrude and Lithgow-Bertelloni (2005a,b).

2.20.2.6 Anisotropy of Minerals in the Earth's Mantle and Core

To understand the anisotropic seismic behavior of polyphase rocks in the Earth's mantle, it is instructive to first consider the properties of the component single crystals. In this section, I will emphasize the anisotropy of individual minerals rather than the magnitude of velocity. The percentage anisotropy (A) is defined here as $A = 200 (V_{\text{maximum}} - V_{\text{minimum}}) / (V_{\text{maximum}} + V_{\text{minimum}})$, where the maximum and minimum are found by exploring a hemisphere of all possible propagation directions. Note that for P-wave velocities, the anisotropy is defined by the maximum and minimum velocities in two different propagation directions, for example, the maximum A is given by the maximum and minimum V_p in a hemisphere or for V_p in two specific directions such as the vertical and horizontal can be used. For S-waves in an anisotropic medium, there are two orthogonally polarized S-waves with different velocities for each propagation direction; hence, A can be defined for each direction. The consideration of the single-crystal properties is particularly important for the transition zone (410–660 km) and lower mantle (below 660 km) as the deformation mechanisms and resulting preferred orientation of these minerals under the extreme conditions of temperature and pressure are very poorly documented by experimental investigations. In choosing the anisotropic single-crystal properties, where possible, I have included the most recent experimental determinations. A major trend in recent years is the use of computational modeling to determine the elastic constants at very high pressures and more recently at high temperatures. The theoretical modeling gives a first estimate of the pressure and temperature derivatives in a range not currently accessible to direct measurement (see review by Karki et al., 2001; also see

Chapter 2.08). Although there is an increasing amount of single-crystal data available to high temperature or high pressure, no data are available for simultaneous high temperature and pressure of the Earth's lower mantle or inner core (see Figure 1 for the pressure and temperatures).

2.20.2.6.1 Upper mantle

The upper mantle (down to 410 km) is composed of three anisotropic and volumetrically important phases: olivine, enstatite (orthopyroxene), and diopside (clinopyroxene). The other volumetrically important phase is garnet, which is nearly isotropic and hence not of great significance to our discussion of anisotropy.

Olivine – A certain number of accurate determinations of the elastic constants of olivine are now available, which all agree that the anisotropy of V_p is 25% and maximum anisotropy of V_s is 18% at ambient conditions for a mantle composition of about Fo90. The first-order temperature derivatives have been determined between 295 and 1500 K for forsterite (Isaak et al., 1989a) and olivine (Isaak, 1992). The first- and second-order pressure derivatives for olivine were first determined to 3 GPa by Webb (1989). However, a determination to 17 GPa by Zaug et al. (1993) and Abramson et al. (1997) has shown that the second-order derivative is only necessary for elastic stiffness modulus C_{55} . The first-order derivatives are in good agreement between these two studies. The second-order derivative for C_{55} has proved to be controversial. Zaug et al. (1993) were the first to measure nonlinear variations of C_{55} with pressure, but other studies have not reproduced this behavior (e.g., for olivine Chen et al., 1996; Zha et al., 1998) or forsterite Zha et al., 1996). The anisotropy of the olivine single crystal increases slightly with temperature (+2%) using the data of Isaak (1992) and reduces slightly with increasing pressure using the data of Abramson et al. (1997).

Orthopyroxene – The elastic properties of orthopyroxene (enstatite or bronzite) with a magnesium number (Mg/(Mg+Fe)) near the typical upper mantle value of 0.9 have also been extensively studied. The V_p anisotropy varies between 15.1% (En80 bronzite; Frisillo and Barsch, 1972) and 12.0% (En100 enstatite; Weidner et al., 1978) and the maximum V_s anisotropy between 15.1% (En80 bronzite; Webb and Jackson, 1993) and 11.0% (En100 enstatite; Weidner et al., 1978). Some of the variation in the elastic constants and anisotropy may be related to composition and structure in the orthopyroxenes (Duffy and Vaughan, 1988). Near-end-member enstatite containing Ca shows only small changes in the bulk and shear moduli by 5% and 3% from the pure Mg end-member (Perrillat et al., 2007). The first-order temperature derivatives have been determined over a limited range between 298 and 623 K (Frisillo and Barsch, 1972). An extended range of temperature derivatives has been given by Jackson et al. (2007) up to 1073 K at ambient pressure. The first- and second-order pressure derivatives for Enstatite have been determined up to 12.5 GPa by Chai et al. (1977b). This study confirms an earlier one of Webb and Jackson to 3 GPa that showed that the first- and second-order pressure derivatives are needed to describe the elastic constants at mantle pressures. The anisotropy of V_p and V_s does not vary significantly with pressure using the data of Chai et al. (1977a) to 12.5 GPa. The anisotropy of V_p and V_s does increase by about 3% when

extrapolating to 1000°C using the first-order temperature derivatives of Frisillo and Barsch (1972).

Clinopyroxene – The elastic constants of clinopyroxene (diopside) of mantle composition have only been experimentally measured at ambient conditions (Collins and Brown, 1998; Levien et al., 1979); both studies show that V_p anisotropy is 29% and V_s anisotropy is between 20% and 24%. There are no measured single-crystal pressure derivatives. In one of the first calculations of the elastic constants of a complex silicate at high pressure, Matsui and Busing (1984) predicted the first-order pressure derivatives of diopside from 0 to 5 GPa. The calculated elastic constants at ambient conditions are in good agreement with the experimental values, and the predicted anisotropy for V_p and V_s of 35.4% and 21.0%, respectively, is also in reasonable agreement. The predicted bulk modulus of 105 GPa is close to the experimental value of 108 GPa given by Levien et al. (1979). The pressure derivative of the bulk modulus 6.2 is slightly lower than the value of 7.8 ± 0.6 given by Bass et al. (1981). Using the elastic constants of Matsui and Busing (1984), the V_p anisotropy decreases from 35.4% to 27.7% and V_s increases from 21.0% to 25.5% with increasing pressure from ambient to 5 GPa. A recent *ab initio* study of the effect of pressure on the elastic constants of diopside and jadeite from 0 to 20 GPa shows a slight decrease in V_p anisotropy from 23.4% to 17.9% and a slight increase in V_s anisotropy from 20.1% to 25.2% (Walker, 2012). Isaak and

Ohno (2003) and Isaak et al. (2005) had measured the temperature derivatives of chrome diopside to 1300 K at room pressure that are notably smaller than other mantle minerals. The single-crystal seismic properties of olivine, enstatite, and diopside at 220 km depth are illustrated in Figure 12. Garnet is nearly isotropic with V_p anisotropy of 0.6% and V_s of 1.3%. The determination of the elastic constants of diopside with upper mantle composition (Collins and Brown, 1998) at ambient pressure agrees closely with values for chrome diopside, except for a 3% decrease in the shear modulus (C_{44}).

2.20.2.6.2 Transition zone

Over the last 20 years, a major effort has been made to experimentally determine the phase petrology of the transition zone and lower mantle. Whereas single crystals of upper mantle phases are readily available, single crystals of transition zone and lower mantle for elastic constant determination have to be grown at high pressure and high temperature. The petrology of the transition zone is dominated by garnet, majorite, wadsleyite, ringwoodite, calcium-rich perovskite, clinopyroxene, and possibly stishovite.

Majorite – The pure Mg end-member majorite of the majorite–pyrope garnet solid solution has tetragonal symmetry and is weakly anisotropic with 1.8% for V_p and 9.1% for V_s (Pacalo and Weidner, 1997). A study of the majorite–pyrope system by Heinemann et al. (1997) shows that tetragonal form

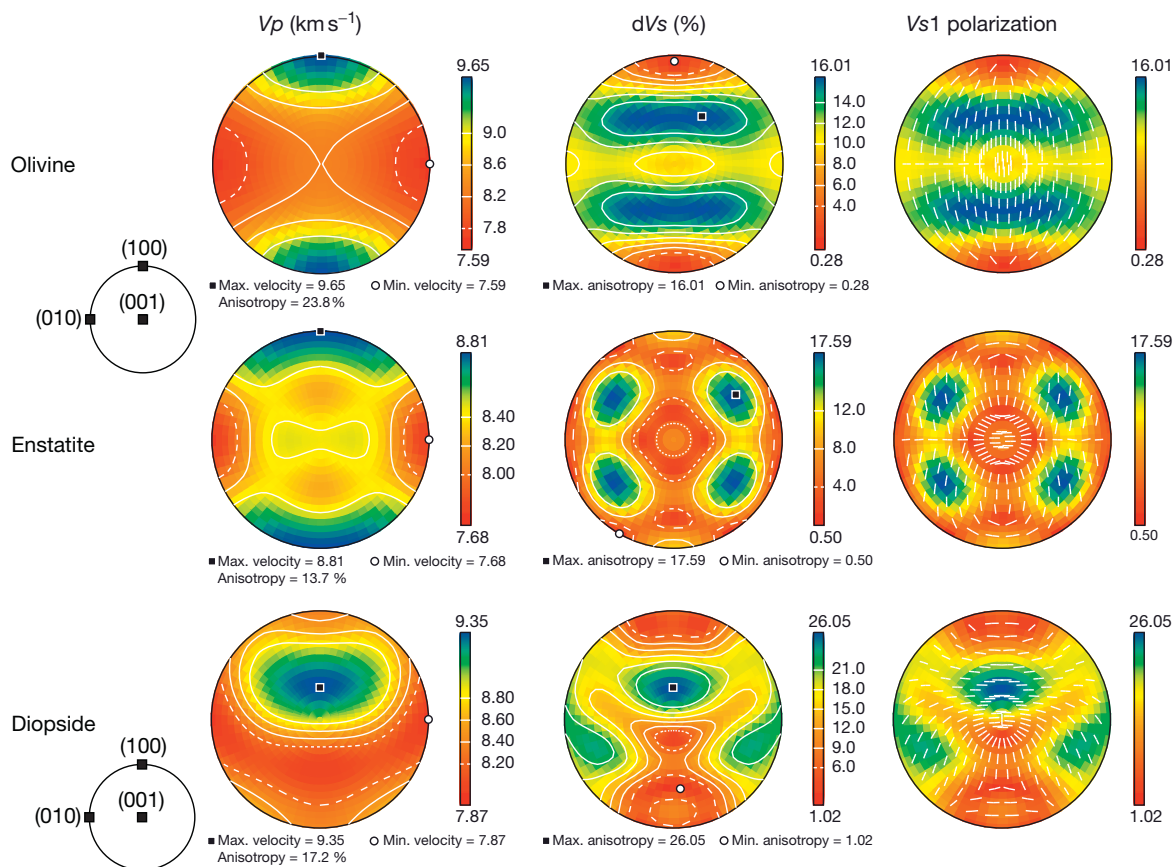


Figure 12 Single-crystal anisotropic seismic properties of upper mantle minerals olivine (orthorhombic), enstatite (orthorhombic), and diopside (monoclinic) at about 220 km (7.1 GPa, 1250 °C).

of majorite is restricted to a composition of less 20% pyrope and hence is unlikely to exist in the Earth's transition zone. Majorite with cubic symmetry is nearly isotropic with V_p anisotropy of 0.5% and V_s of 1.1%. Pressure derivatives for majorite and majorite–pyrope have been determined by Sinogeikin and Bass (2002a) and temperature derivatives by the same authors (2002b). Cubic majorite has very similar properties to pyrope garnet (Chai et al., 1997a) as might be expected. The elastic properties of sodium-rich majorite have been studied by Reichmann et al. (2002).

Wadsleyite – The elastic constants of Mg_2SiO_4 wadsleyite were first determined by Sawamoto et al. (1984), and this early determination was confirmed by Zha et al. (1997) with a V_p anisotropy of 16% and V_s of 17%. The $(\text{Mg,Fe})_2\text{SiO}_4$ wadsleyite has slightly lower velocities and higher anisotropies (Sinogeikin et al., 1998). The first-order pressure derivatives determined from the data of Zha et al. (1997) to 14 GPa show that the anisotropy of Mg_2SiO_4 wadsleyite decreases slightly with increasing pressure. At pressures corresponding to the 410 km seismic discontinuity (ca. 13.8 GPa), the V_p anisotropy would be 11.0% and V_s 12.5%.

Ringwoodite – The elastic constants of Mg_2SiO_4 ringwoodite were first measured by Weidner et al. (1984) and $(\text{Mg,Fe})_2\text{SiO}_4$ ringwoodite by Sinogeikin et al. (1998) at ambient conditions with V_p anisotropy of 3.6 and 4.7% and V_s of 7.9 and 10.3%, respectively. Kiefer et al. (1997) had calculated the elastic constants of Mg_2SiO_4 ringwoodite to 30 GPa. Their constants at ambient conditions give a V_p anisotropy of 2.3% and V_s of 4.8% very similar to the experimental results of Weidner et al. (1984). There is a significant variation (5–0%) of the anisotropy of ringwoodite with pressure 15 GPa (ca. 500 km depth), the V_p anisotropy is 0.4%, and V_s is 0.8%; hence, ringwoodite is nearly perfectly isotropic at transition zone pressures. Single-crystal temperature derivatives have

been measured for ringwoodite (Jackson et al., 2000; Sinogeikin et al., 2001), but none are available for wadsleyite. Olivine transforms to wadsleyite at about 410 km, and wadsleyite transforms to ringwoodite at about 500 km; both transformations result in a decrease in anisotropy with depth. The gradual transformation of clinopyroxene to majorite between 400 and 475 km would also result in a decrease in anisotropy with depth. The seismic anisotropy of wadsleyite and ringwoodite is illustrated in Figure 13. An *ab initio* molecular dynamics study by Li et al. (2006a) has shown that ringwoodite is nearly isotropic at transition zone conditions with P- and S-wave anisotropies close to 1%; extrapolated experimental values to a depth of 550 km (19.1 GPa, 1520 °C) suggest that the V_p anisotropy and V_s anisotropy are 3.3% and 8.2%.

2.20.2.6.3 Lower mantle

The lower mantle is essentially composed of perovskite, ferropericase, and possibly minor amount of SiO_2 in the form of stishovite in the top part of the lower mantle (e.g., Ringwood, 1991). Ferropericase is the correct name for $(\text{Mg,Fe})\text{O}$ with small percentage of iron, less than 50% in Mg site; previously, this mineral was incorrectly called magnesio-wüstite, which should have more than 50% Fe. It is commonly assumed that there is about 20% Fe in ferropericase in the lower mantle. MgSiO_3 may be in the form of perovskite or possibly ilmenite. The ilmenite-structured MgSiO_3 is most likely to occur at the bottom of the transition zone and the top of the lower mantle. In addition, perovskite transforms to postperovskite in the D'' layer, although exact distribution with depth (or pressure) of the phases will depend on the local temperature and their iron content.

Perovskite (MgSiO_3 and CaSiO_3) – The first determination of the elastic constants of pure MgSiO_3 perovskite at ambient conditions was given by Yeganeh-Haeri et al. (1989). However,

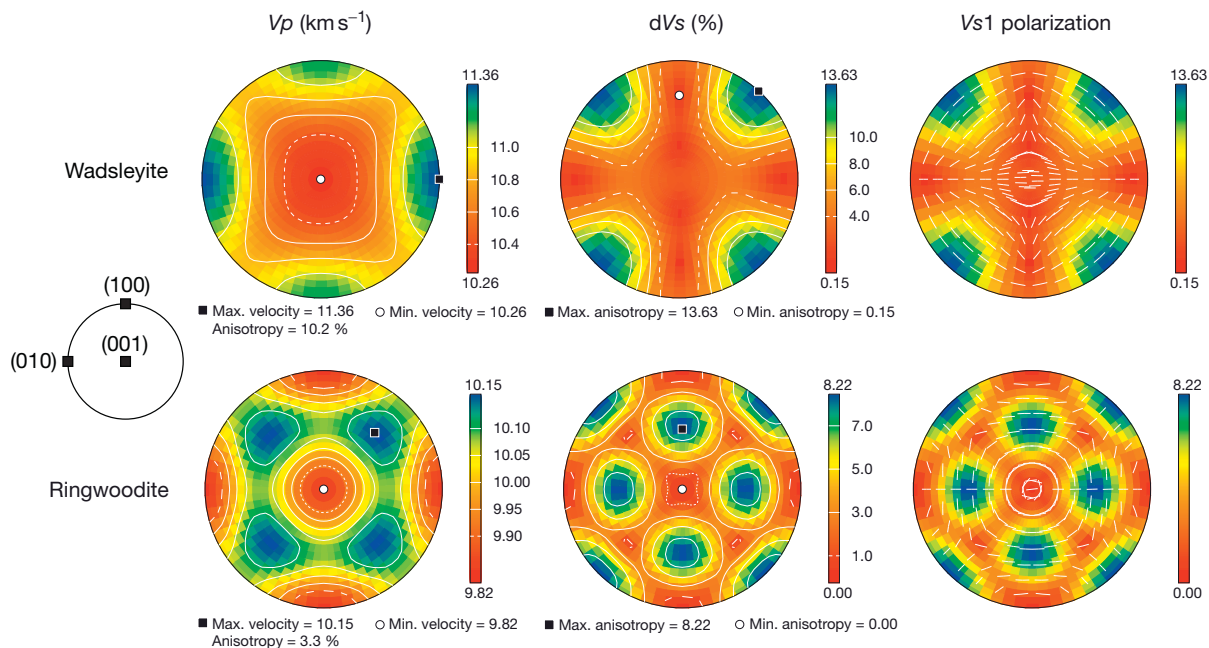


Figure 13 Single-crystal anisotropic seismic properties of transition zone minerals wadsleyite (orthorhombic) at about 450 km (15.2 GPa, 1450 °C) and ringwoodite (cubic) at about 550 km (19.1 GPa, 1520 °C).

this determination has been replaced by a more accurate study of a better quality crystal (Yeganeh-Haeri, 1994). The 1994 study gives V_p anisotropy of 13.7% and V_s of 33.0%. The [010] direction has the maximum dVs anisotropy. A new measurement of the elastic constants of MgSiO_3 perovskite at ambient conditions was made by Sinogeikin et al. (2004) and gives V_p anisotropy of 7.6% and dVs of 15.4%, which has a very similar velocity distribution to the determination of Yeganeh-Haeri (1994), but the anisotropy is reduced by a factor of 2. Karki et al. (1997a) calculated the elastic constants of MgSiO_3 perovskite 140 GPa at 0 K. The calculated constants are in close agreement with the experimental measurements of Yeganeh-Haeri (1994) and Sinogeikin et al. (2004). Karki et al. (1997a) found that significant variations in anisotropy occurred with increasing pressure, first decreasing to 6% at 20 GPa for V_p and to 8% at 40 GPa for V_s and then increasing to 12% and 16%, respectively, at 140 GPa. At the 660 km seismic discontinuity (ca. 23 GPa), the V_p and V_s anisotropies would be 6.5% and 12.5%, respectively. Recent progress in finite temperature first-principles methods for elastic constants has allowed their calculation at lower mantle pressures and temperatures. Oganov et al. (2001) calculated the elastic constants of Mg-perovskite at two pressures and three temperatures for the lower mantle (Figure 14). More recently, Wentzcovitch et al. (2004) had calculated the elastic constants over the complete range of lower mantle conditions and produced pressure and temperature derivatives. The results for pure Mg-perovskite from Oganov et al. and Wentzcovitch et al. agree quite closely for P-wave anisotropy, but Oganov's elastic constants give a higher S-wave anisotropy. At ambient conditions, the results from all studies are very similar with the V_p anisotropy that is 13.7% and the V_s anisotropy that is 33.0%. When extrapolated along a geotherm using the pressure and temperature derivatives of Wentzcovitch et al. (2004), the P- and S-wave anisotropies about the same at 8% at 1000 km

depth and again similar anisotropies of 13% at 2500 km depth. The plasticity of Mg-perovskite has been studied using *ab initio* dislocation modeling to determine the critical resolved shear stresses at lower mantle pressures and viscoplastic self-consistent (VPSC) modeling (Mainprice et al., 2008a). Using the VPSC-predicted CPO and *ab initio* elastic constants of Oganov et al. (2001), the predicted anisotropy at lower mantle pressures and temperatures is weak (>3% for P-waves and >2% for S-waves) and decreases with increasing temperature and pressure.

The other perovskite structure present in the lower mantle is CaSiO_3 perovskite; recent *ab initio* molecular dynamics study by Li et al. (2006b) has shown that this mineral is nearly isotropic at lower mantle conditions with P- and S-wave anisotropies close to 1%. Recent extension of experimental measurements to *in situ* lower mantle conditions and more refined *ab initio* modeling at finite temperature are starting to challenge previous results. The measurement of sound velocities at lower mantle conditions by Murakami et al. (2012) suggests that the lower mantle is composed of 93% Mg-perovskite. However, a state-of-the-art *ab initio* modeling of Mg-perovskite elastic properties (Zhang et al., 2013) with the current view of a pyrolite mantle composition for lower mantle provides an alternative view. The work of Zhang et al. (2013) also allows a better understanding of the P- and S-wave anisotropies along geotherms at 1500, 2500, and 3500 K. In Figure 15, you can see that for P-wave anisotropy, there is little effect of temperature and the anisotropy increases with depth. For S-wave, there is strong increase of anisotropy with temperature and depth. Mg-perovskite may be playing more important role in the seismic anisotropy of the D'' layer than we have considered so far.

MgSiO₃ ilmenite – Experimental measurements by Weidner and Ito (1985) have shown that MgSiO₃ ilmenite of trigonal symmetry is very anisotropic at ambient conditions with V_p anisotropy of 21.1% and V_s of 36.4%. Pressure derivatives to

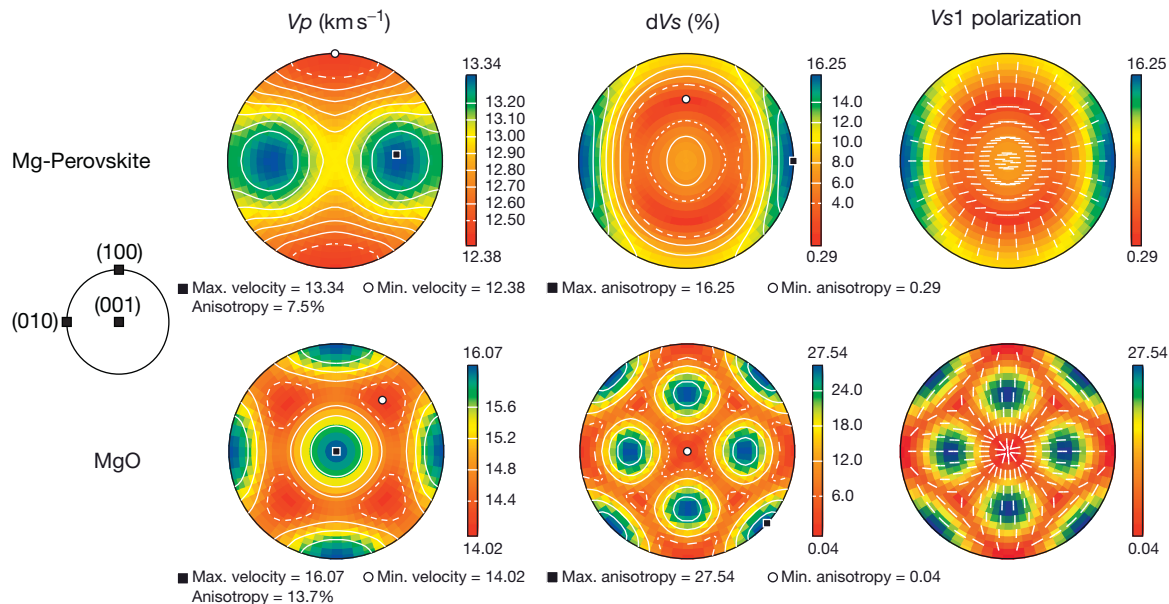


Figure 14 Single-crystal anisotropic seismic properties of lower mantle minerals Mg-perovskite (orthorhombic) and MgO (pericline – cubic) at about 2000 km (88 GPa, 3227 °C) using the elastic constants determined at high P – T by Oganov et al. (2001) and Karki et al. (2000), respectively.

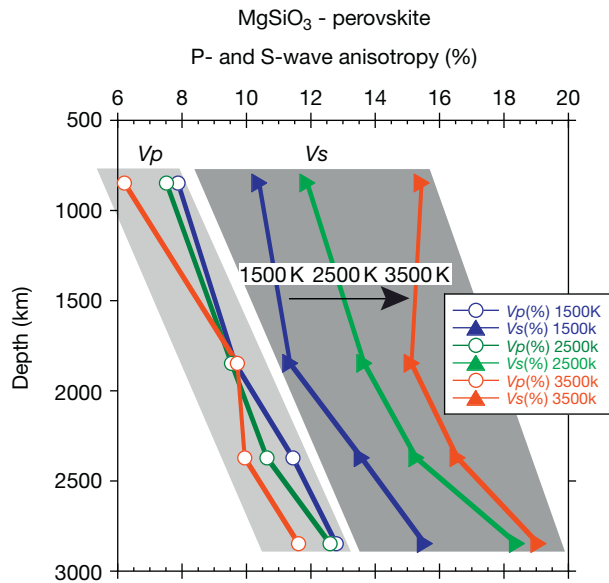


Figure 15 P- and S-wave seismic anisotropy for MgSiO_3 perovskite with depth in the lower mantle predicted by the *ab initio* calculations of Zhang et al. (2013).

30 GPa have been obtained by first-principles calculation (Da Silva et al., 1999) and the anisotropy decreases with increasing pressure to 9.9% for P-waves and 24.8% for S-waves at 30 GPa.

Ferropervicase – The other major phase is ferropervicase ($\text{Mg,Fe})\text{O}$, for which the elastic constants have been determined. The elastic constants of the pure end-member pericase MgO of the MgO – FeO solid solution series have been measured to 3 GPa by Jackson and Niesler (1982). Isaak et al. (1989a) had measured the temperature derivatives for MgO to 1800 K. Both these studies indicate a V_p anisotropy of 11.0% and V_s of 21.5% at ambient conditions. Karki et al. (1997a,b,c) calculated the elastic constants of MgO to 150 GPa at 0 K. The thermoelasticity of MgO at lower mantle temperatures and pressures has been studied by Isaak et al. (1990) and Karki et al. (1999, 2000) (Figure 16), and more recently Sinogeikin et al. (2004, 2005); there is good agreement between these studies for the elastic constants and pressure and temperature derivatives. However, the theoretical studies do not agree with experimentally measured cross pressure–temperature derivatives of Chen et al. (1998). At the present time, only the theoretical studies permit the exploration of the seismic properties of MgO at lower mantle conditions. They find considerable changes in anisotropy preserved at high temperature with increasing pressure, along a typical mantle geotherm; MgO is isotropic near the 670 km discontinuity, but the anisotropy of P- and S-waves increases rapidly with depth reaching 17% for V_p and 36% for V_s at the D'' layer. The anisotropy of MgO increases linearly from 11.0% and 21.5% for V_p and V_s , respectively, at ambient conditions to 20% and 42%, respectively, at 1800 K according to the data of Isaak et al. (1989a,b). The effect of temperature on anisotropy is more important at low pressure than at lower mantle pressures, where the effect of pressure dominates according to the results of Karki et al. (1999). Furthermore, not only the magnitude of the anisotropy of MgO but also the orientation of the anisotropy

changes with increasing pressure according to the calculations of Karki et al. (1999), for example, the fastest V_p is parallel to [111] at ambient pressure and becomes parallel to [100] at 150 GPa pressure and fastest S-wave propagating in the [110] direction has a polarization parallel to [001] at low pressure that changes to [1–10] at high pressure.

Ferropervicase – Magnesiowüstite solid solution series has been studied at ambient conditions by Jacobsen et al. (2002); for ferropervicase with 24% Fe, the P-wave anisotropy is 10.5% and maximum S-wave is 23.7%, slightly higher than pure MgO at the same conditions. Data are required at lower mantle pressures to evaluate if the presence of iron has a significant effect on anisotropy of ferropervicase of mantle composition. The effect of anomalous compressibility of ferropervicase through the iron spin crossover has been studied experimentally at room temperature and high pressure; in these conditions, the high to low spin produces a sharp reduction in C_{11} and C_{12} elastic moduli (e.g., Marquardt et al., 2009). Theoretical studies using *ab initio* methods (e.g., Wentzcovitch et al., 2009) at lower mantle conditions show that the change in elasticity is smaller and occurs in a broad depth range of 1200–2000 km for 2000 K geotherm. The elastic anomaly is increasingly attenuated with higher temperatures. It has been suggested that iron spin crossover would be seismically transparent (Antonangeli et al., 2011). It should be noted that iron spin crossover has also been proposed for perovskite, this crossover has much weaker effect on elastic properties as shown by experimental studies (e.g., Lundin et al., 2008), and *ab initio* modeling of the elastic properties (Caracas et al., 2010) suggests this will be difficult to detect seismically.

SiO_2 polymorphs – The free SiO_2 in the transition zone and the top of the lower mantle (to a depth of 1180 km or 47 GPa) will be in the form of stishovite. The original experimental determination of the single-crystal elastic constants of stishovite by Weidner et al. (1982) and the more recent calculated constants of Karki et al. (1997b) both indicate V_p and V_s anisotropies at ambient conditions of 26.7–23.0% and 35.8–34.4%, respectively, making this a highly anisotropic phase. The calculations of Karki et al. (1997a,b,c) show that the anisotropy increases dramatically as the phase transition to CaCl_2 -structured SiO_2 is approached at 47 GPa. The V_p anisotropy increases from 23.0% to 28.9% and V_s from 34.4% to 161.0% with increasing pressure from ambient to 47 GPa. The maximum V_p is parallel to [001] and the minimum parallel to [100]. The maximum dV_s is parallel to [110] and the minimum parallel to [001]. I discuss the properties of stishovite in the section on subduction zones.

Postperovskite – Finally, this new phase is present in the D'' layer. Discovered and published in May 2004 by Murakami et al. (2004), the elastic constants at 0 K were rapidly established at low (0 GPa) and high (120 GPa) pressure by static atomistic calculations (Iitaka et al., 2004; Oganov and Ono, 2004; Tsuchiya et al., 2004). From these first results, we can see that Mg-postperovskite is very different to Mg-perovskite as there are substantial changes in the distribution of the velocity anisotropy with increasing pressure (Figure 16). At zero pressure, the anisotropy is very high, 28% and 47% for P- and S-waves, respectively. The maximum for V_p is parallel to [100] with small submaxima parallel to [001] and minimum near [111]. The shear wave splitting (dV_s) has maxima

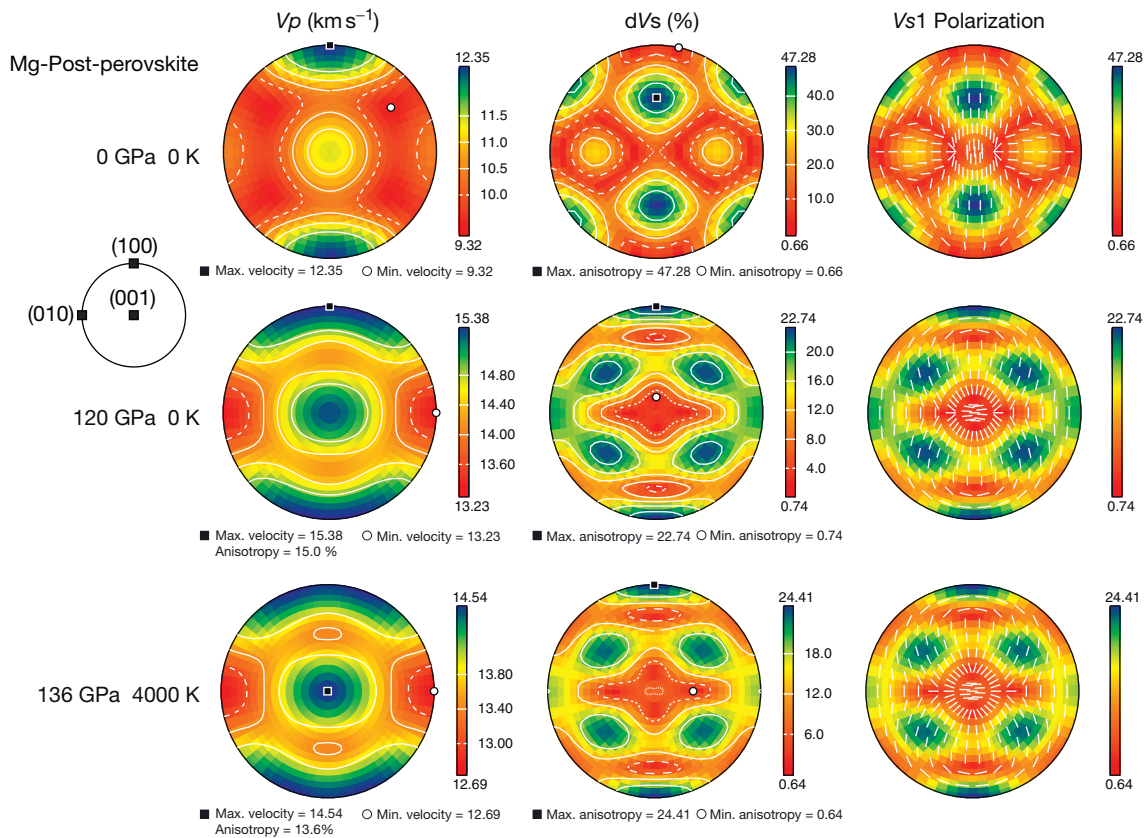


Figure 16 Single-crystal anisotropic seismic properties of the D'' layer mineral Mg-postperovskite (orthorhombic). Increasing the pressure from 0 to 120 GPa at a temperature of 0 K decreases the anisotropy and also changes the distribution the maximum velocities and S-wave polarizations. Elastic constants calculated by Tsuchiya et al. (2004). Increasing the pressure to 136 GPa and temperature to 4000 K, there are relatively minor changes in the anisotropy. Elastic constants calculated by Stackhouse et al. (2005).

parallel to $\langle 101 \rangle$ and $\langle 110 \rangle$. At 120 GPa, the anisotropy has reduced to 15% and 22% for P- and S-waves, respectively. The distribution of velocities has changed, with the P maximum still parallel to $[100]$ and submaximum parallel to $[001]$, which is now almost the same velocity as parallel to $[100]$; the minimum is now parallel to $[010]$. The S-wave splitting maxima have also changed and are now parallel to $\langle 111 \rangle$. Apparently, the compression of the postperovskite structure has caused important elastic changes as in MgO. An *ab initio* molecular dynamics study by Stackhouse et al. (2005) at high temperature revealed that the velocity distribution and anisotropy were little effected by increasing the temperature from 0 to 4000 K when at a pressure of 136 GPa (Figure 16). Wentzcovitch et al. (2006) produced a more extensive set of high-pressure elastic constants and pressure and temperature derivatives, similar P distributions, and slightly different shear wave splitting pattern with maximum along the $[001]$ axis that is not present in the Stackhouse et al. velocity surfaces or in high pressure 0 K results.

In conclusion, for the mantle, we can say that the general trend favors an anisotropy decrease with increasing pressure and increase with increasing temperature; olivine is a good example of this behavior for minerals in upper mantle and transition zone. The changes are limited to a few percent in most cases. The primary causes of the anisotropy changes are minor crystal structural rearrangements rather than velocity changes due to

density change caused by compressibility with pressure or thermal expansion with temperature. The effect of temperature is almost perfectly linear in many cases; some minor nonlinear effects are seen in diopside, MgO, and SiO₂ polymorphs. There may be some perturbation in the seismic anisotropy due to the iron spin crossover around 1200–2000 km. Nonlinear effects with increasing pressure on the elastic constants cause the anisotropy of wadsleyite and ringwoodite to first decrease. In the case of the lower mantle minerals Mg-perovskite and MgO, there is a steady increase in the anisotropy in increasing depth; this is a very marked effect for MgO. Stishovite also shows major changes in anisotropy in the pressure range close to the transformation to the CaCl₂ structure. The single-crystal temperature derivatives of wadsleyite, ilmenite MgSiO₃, and stishovite are currently unknown, which makes quantitative seismic anisotropic modeling of the transition zone and upper part of the lower mantle speculative. To illustrate the variation of anisotropy as a function of mantle conditions of temperature and pressure, I have calculated the seismic properties along a mantle geotherm (Figure 17). The mantle geotherm is based on the PREM model for the pressure scale. The temperature scale is based on the continental geotherm of Mercier (1980) from the surface to 130 km and Ito and Katsura (1989) for the transition zone and Brown and Shankland (1981) for the lower mantle. The upper mantle minerals olivine (V_p , V_s) and enstatite (V_p) show a slight increase of anisotropy in the first 100 km due to the effect of

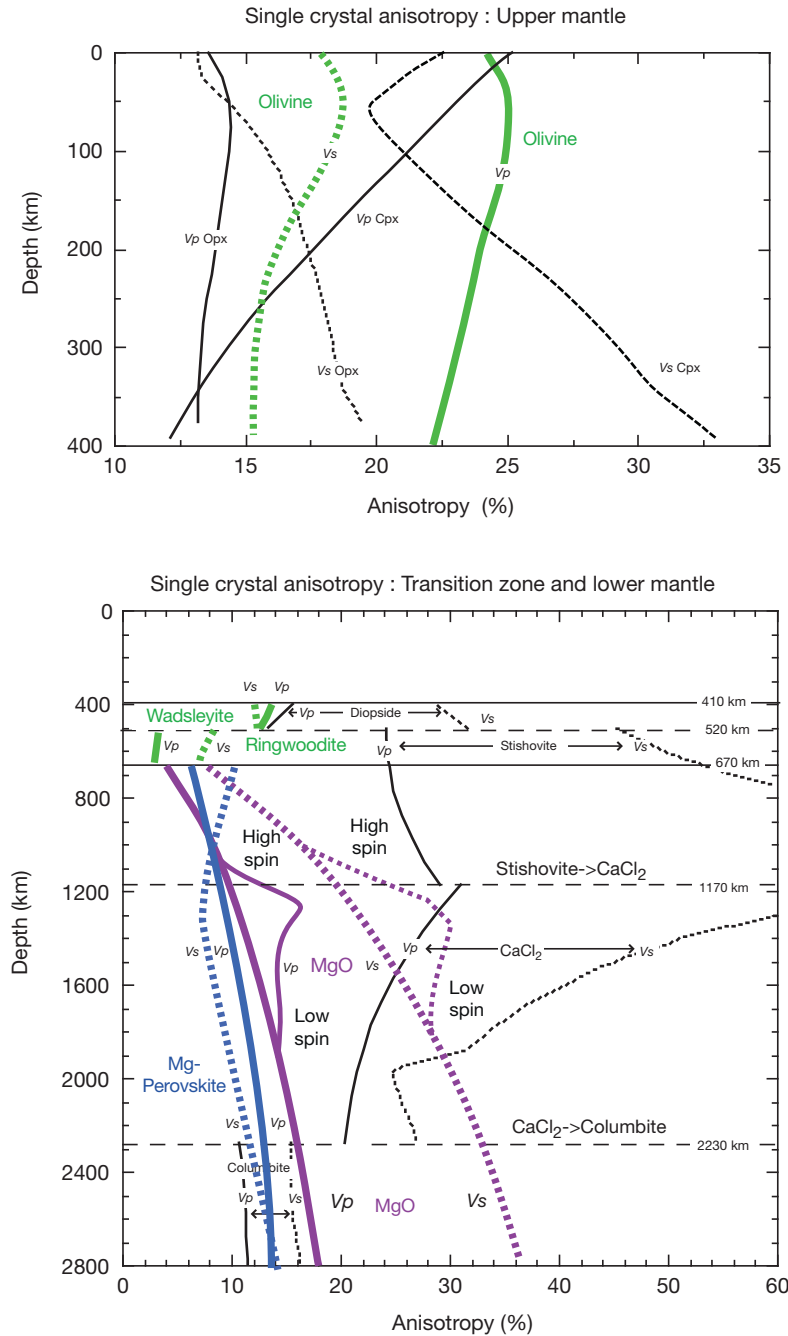


Figure 17 Variation of single-crystal seismic anisotropy with depth. The phases with important volume fractions (see Figure 1) (olivine, wadsleyite, ringwoodite, Mg-perovskite, and MgO) are highlighted by a thicker line. P-wave anisotropy is the full line and the S-wave is the dashed line. See text for details.

temperature. With increasing depth, the trend is for decreasing anisotropy except for V_s of enstatite and diopside. In the transition zone and lower mantle, the situation is more complex due to the presence of phase transitions. In the transition zone, diopside may be present to about 500 km with an increasing V_s and decreasing V_p anisotropy with depth. Wadsleyite is less anisotropic than olivine at 410 km, but significantly more anisotropic than ringwoodite found below 520 km. Although the lower mantle is known to be seismically isotropic, the

constituent minerals are anisotropic. MgO shows important increase in anisotropy with depth (10–30%) at 670 km (it is isotropic) and 2800 km (it is very anisotropic), possibly being candidate mineral to explain anisotropy of the D'' layer. Mg-perovskite is strongly anisotropic (ca. 10%) throughout the lower mantle, but now, it is strongest in the lowermost mantle (Zhang et al., 2013). The SiO_2 polymorphs are all strongly anisotropic, particularly for S-waves. If free silica is present in the transition zone or lower mantle, due perhaps to the presence

of subducted basalt (e.g., Ringwood, 1991), then even a small volume fraction of the SiO_2 polymorphs could influence the seismic anisotropy of the mantle. However, to do so, the SiO_2 polymorphs would have to be oriented, due to either dislocation glide (plastic flow), oriented grain growth, or anisometric crystal shape (viscous flow) (e.g., Mainprice and Nicolas, 1989). Given that the SiO_2 polymorphs are likely to be less than 10% by volume (Ringwood, 1991) and hence would not be the load-bearing framework of the rock, it is more likely that the inequant shape of SiO_2 polymorphs would control their orientation during viscous flow.

2.20.2.6.4 Subduction zones

Subduction zones are mainly vertical structures in the Deep Earth, with a major section in the upper mantle and transition zone. In certain regions, the subducted plates have nearly horizontal sections just below 670 km seismic discontinuity. Slabs continue to descend until they reach the D'' layer and CMB. During the descent of a plate, the mineralogy changes almost continuously with the temperature and pressure changes. The subducted plate is populated with many very specific minerals because the temperature of the plate is generally lower than the surrounding mantle, whereas the depth controls the pressure. The subducting plate is a major vector for chemical exchange with deep Earth, not only hydrated minerals providing hydrogen but also minerals derived from sediments and oceanic basalts rich in potassium, sodium, aluminum, and silicon. Subduction zones are also the most seismically active regions of the planet.

Here, we will focus on the seismic anisotropy of a few key subduction zone minerals. The upper part of the subduction zone is dominated by the mantle wedge, where dehydration of the plate and fluid-triggered melting are very active processes, which are directly associated with earthquake activity and volcanism, respectively. One of the reactions occurring within the mantle wedge is hydration of minerals by fluids released from the descending slab, for example, the transformation of olivine to the high-pressure serpentine mineral antigorite. Bezacier et al. (2010) had reported experimental measurements of antigorite single-crystal elasticity at ambient conditions. Antigorite is monoclinic layered-structured mineral that has fast V_p in the (001) plane and low V_p normal to it. V_{s1} is fast in the (001) plane with a polarization parallel to the (001) plane, whereas V_{s2} is slow in the (001) plane with a polarization normal to the (001) plane. The V_p and V_s anisotropies are high at 47% and 75%, respectively, with the highest S-wave splitting in the (001) plane (Figure 18). One key seismic observation in the mantle wedge because of the presence of fluids is the V_p/V_s ratio; for anisotropic crystals, there are two ratios, V_p/V_{s1} and V_p/V_{s2} , where V_p/V_{s1} corresponds to ratio with the first S-wave arrival and is probably the most frequently measured. V_p/V_{s1} ranges from 2.3 to 1.1 with direction, being highest normal and lowest parallel to the (001) plane. V_p/V_{s2} range is 3.8–1.4, the magnitude being highest parallel and lowest normal to the (001) plane, that is, opposite in distribution to V_p/V_{s1} ; hence, measuring V_p/V_{s2} , V_p/V_{s1} could provide a complementary set of data. All the velocity-related properties just described are typical of layered-structured minerals in widest sense or phyllosilicates in the present case. Information on the pressure dependence of antigorite has been provided by

an *ab initio* study by Mookherjee and Capitani (2011) up to 13.8 GPa, and more recently, an experimental study by Bezacier et al. (2013) measured a subset of the moduli to 9 GPa. Bezacier et al. (2013) indicated that there is decrease in P- and S-wave anisotropies from 47% to 75%, respectively, at ambient conditions to 22% and 63% at 7 GPa. Mookherjee and Capitani (2011) found that V_p anisotropy is 57% at zero pressure and that it decreases to 27% at 7 GPa; however, V_s anisotropy is 54% at zero pressure and increases to 63% at 7 GPa, so that both studies agree at 7 GPa, but not ambient conditions. Another potential mantle wedge mineral that has stable higher-temperature conditions than antigorite is talc; this industrially very important mineral has been studied using *ab initio* methods by Mainprice et al. (2008b). At zero pressure, talc is very anisotropic with P- and S-wave anisotropies of 80% and 85%, respectively; with increasing pressure, both P- and S-wave anisotropies decrease. At pressures where talc is known to be stable in the Earth (up to 5 GPa), the V_p and V_s anisotropies are reduced to about 40% for both velocities, which is still a very high value. The third important layered-structured mineral is chlorite; Mookherjee and Mainprice (2014) have studied the elastic properties to a pressure of 18.4 GPa. Chlorite is stable to higher temperatures and pressures than antigorite and talc. Chlorite has velocity characteristics very similar to antigorite, with P- and S-wave anisotropies of 30% and 52%, respectively, at zero pressure, which decrease with pressure for P-waves to 25% but increase with pressure for S-waves to 72%. Antigorite can often be seen associated with chlorite as intergrowths with the same crystal orientation (e.g., Morales et al., 2013); there are also topotactic relationships between antigorite and olivine during the phase transformation (Boudier et al., 2010; Morales et al., 2013). Both antigorite and chlorite contain 13 wt.% H_2O , and hence, they are more important for the water cycle than talc, which has only 4.8 wt.% H_2O . All these layered-structured minerals form CPO with strong point maximum of the (001) normal to the foliation and girdles of both (100) and (010) in the foliation plane, which will result in very strong transverse isotropic velocity distribution.

At greater depths and higher pressures, there is transition to the 10 Å phase (13 wt.% H_2O) followed with increasing depth by a series of dense hydrogen magnesium silicate (DHMS) or alphabet phases. The DHMSs have only to be observed in laboratory experiments, but hypothetically could exist along a cold slab geotherm (e.g., Mainprice and Ildefonse, 2009), and mainly present at depths of the mantle transition zone. Sanchez-Valle et al. (2006, 2008) had studied the elasticity of the phase A (12 wt.% H_2O) in the laboratory at pressures up to 12.4 GPa. The velocity distribution is very different to the layered-structured minerals described earlier with fast V_p normal to (0001) and slow V_p in the (0001); V_{s1} is slow in the (0001) plane, the polarization parallel to the (0001) plane, and the maximum V_{s1} at 45° to the (0001) plane; and V_{s2} also is slow normal to the (0001) and but fast normal to the (0001) plane. The P- and S-wave anisotropies are quite modest at 9% and 18%, respectively, at 9 GPa in the stability field of this mineral. Pressure has only a very modest effect on the anisotropy of phase A. The phase D is the DHMS that occurs at the greatest pressures and depths; being stable below 670 km discontinuity, it is the only mineral to potentially recycle

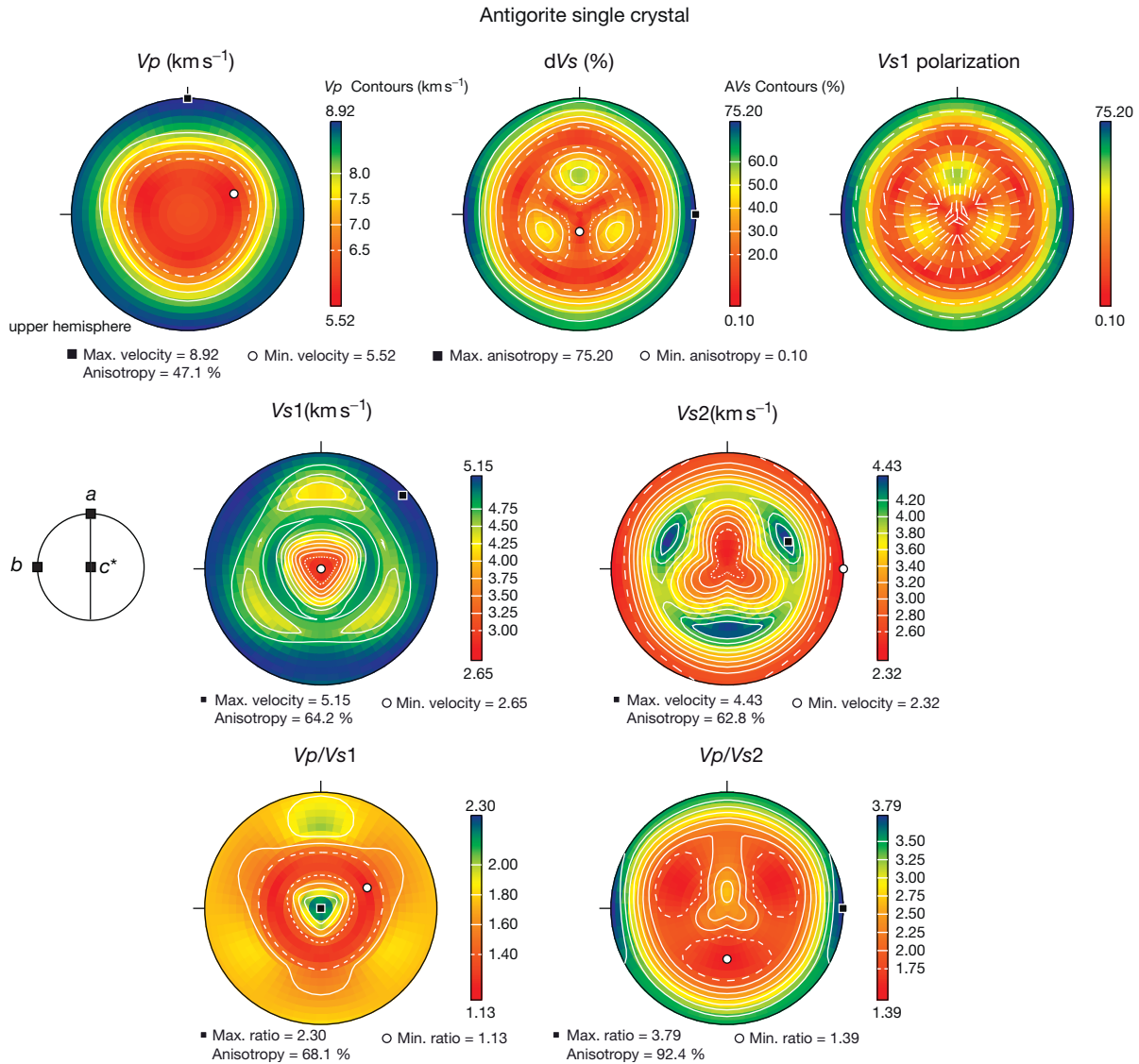


Figure 18 The seismic properties of a single crystal of antigorite at room pressure (Bezacier et al., 2010). V_p and V_{s1} are both fast in the basal plane (normal to c^*). V_{s1} polarization is parallel to the basal plane. V_{s2} is fast in directions inclined to the basal plane. V_p/V_{s1} has the maximum normal to the basal plane, whereas V_p/V_{s2} is highest parallel to the basal plane. Antigorite is monoclinic, so the plane normal to b and b^* is a mirror plane (black vertical line containing a and c^*). Note that there is some imperfect threefold symmetry.

hydrogen into the lower mantle. It is a candidate mineral for horizontal or stagnant slabs. The elasticity of phase D has been measured experimentally at ambient conditions (Rosa et al., 2012) for Mg- and Al-Fe-bearing crystals. Using *ab initio* methods, the elasticity of the phase D has been studied by Mainprice et al. (2007) to 84 GPa and as function of hydrogen bond symmetrization by Tsuchiya and Tsuchiya (2008) to 60 GPa. The phase D has a velocity distribution that has more in common with a layered-structured mineral than the phase A. The P-wave velocity is fast in (0001) plane and slow normal to the (0001) plane. V_{s1} is fast in the basal plane and polarized parallel to the (0001) plane and V_{s2} is the opposite. At ambient conditions, the P- and S-wave anisotropies are 18% and 19%, and the agreement between experimental and theoretical values is very good. At pressure of 24 GPa in the stability field of phase D, the anisotropies of P- and S-waves are 9%

and 18%, respectively, showing a decrease for the P-wave anisotropy with increasing pressure. The spin transition of Fe^{3+} in Al-bearing phase D occurs at around 40 GPa (Chang et al., 2013) and causes a decrease in bulk modulus from 253 to 147 GPa. The decrease in bulk modulus corresponds to bulk sound velocity drop of 2 km s^{-1} , which could explain the exceptionally strong small-scale heterogeneity detected by direct P-waves in the mid-lower mantle beneath the circum-Pacific subduction zones (e.g., Kaneshima and Helffrich, 2010), a region with horizontal slabs below 670 km discontinuity. A recent study using first-principles methods has predicted a new DHMS form from breakdown of the phase D to give MgSiO_4H_2 plus stishovite (Tsuchiya, 2013) at pressure of about 40 GPa; at the present time, there is no experimental confirmation of this new phase. Finally, comparison with brucite $\text{Mg}(\text{OH})_2$ is interesting as it is a model system for

understanding DHMS under hydrostatic compression and an important structural unit of many layer silicates, such as chlorite, antigorite, and talc. The single-crystal elastic constants of brucite have been measured to a pressure of 15 GPa by Jiang et al. (2006). The seismic anisotropy of brucite is exceptionally high at ambient conditions with P-wave and S-wave anisotropies of 57% and 46%, respectively. Both forms of anisotropy decrease with increasing pressure being 12% and 24% at 15 GPa for P-wave and S-wave anisotropies, respectively. The stronger decrease of P-wave anisotropy compared to S-wave is probably related to the very important linear compressibility along the c -axis. The apparent symmetry of the seismic anisotropy of brucite changes with pressure (Figure 19). Brucite is stable to 80 GPa and modest temperatures, so it could be an anisotropic component of cold subducted slabs. A mineral called the phase X, which occurs as hydrous and anhydrous forms and is stable at transition zone pressures and temperatures, could contribute to mineralogy of slabs. The phase X is the reaction product of the breakdown of potassium rich amphibole (K-richterite) (Konzett and Fei, 2000). The elastic properties of the phase X have been predicted by *ab initio* methods to a pressure of 30 GPa (Mookherjee and Steinle-Neumann, 2009a). The anhydrous phase X has hexagonal symmetry (space group $P6_3cm$); hence, it has the equivalent elastic symmetry to a transverse isotropic sample. At transition zone pressure of 22 GPa, anhydrous phase X has P- and S-wave anisotropies of 13.1% and 12.2%, respectively.

In addition to these hydrous phases, some of normally anhydrous minerals in the subducted slab can become hydrated to a limited degree; the important ones in terms of volume fraction are olivine, wadsleyite, and ringwoodite for the pyrolite mantle (Figure 1). For the upper mantle, olivine is the most important mineral being between 50% and 70% by

volume of a typical mantle peridotite. Single-crystal elastic constants for forsterite and olivine with 0.9 and 0.8 wt.% water have been measured by Jacobsen et al. (2008, 2009) at ambient conditions; 0.9 wt.% water is considered the maximum water storage capacity for olivine (Smyth et al., 2006). The combined effect of 3 mol% Fe and 0.8 wt.% water causes a reduction of the bulk and shear moduli of 2.9% and 4.5%, respectively. Greater modulus reductions are expected for more iron-rich than Fo90 olivine mantle compositions. New measurements for forsterite with 0.9 wt.% water to 14 GPa (Mao et al., 2010) reveal some unexpected behavior with pressure. Below ~ 3.5 GPa, the V_p and V_s of hydrous forsterite are slower than anhydrous crystal by 0.6% and 0.4%, respectively, whereas above this pressure range, the hydrous crystal has faster velocities by 1.1% and 1.9%, respectively. At room pressure, the P- and S-wave anisotropies are, respectively, 24.7% and 18.0% for anhydrous forsterite and 23.9% and 17.8% for hydrous forsterite, indicating a decrease of 0.8% and 0.2% upon hydration. At 14 GPa, the P- and S-wave anisotropies are, respectively, 21.2% and 13.5% for anhydrous forsterite and 15.4% and 12.1% for hydrous forsterite, indicating a decrease of 6.0% and 1.4% upon hydration. Hence, the main effect of hydration on olivine elasticity is a change of velocity and reduction of P-wave anisotropy and almost no effect on S-wave anisotropy.

In the transition zone (410–670 km depth), the high-pressure polymorphs of olivine, wadsleyite, and ringwoodite, in their hydrous forms, have the potential to store more water as hydroxyl than the oceans on the Earth's surface (e.g., Jacobsen, 2006). Wadsleyite and ringwoodite can be synthesized with up to 3.1 and 2.8 wt.% H_2O , respectively, which is nearly three times that of olivine. The maximum water solubility in wadsleyite at transition zone conditions

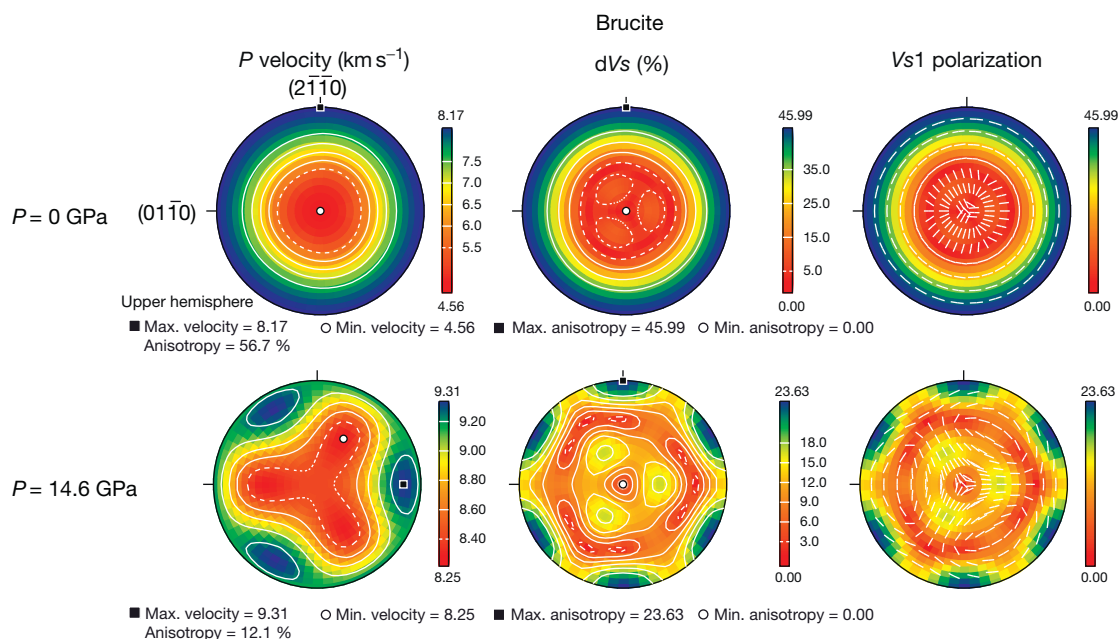


Figure 19 Single-crystal anisotropic seismic properties of brucite (trigonal) at 0 and 14.6 GPa (data from Jiang et al., 2006). Note the change in velocity distribution of P-waves, dV_s anisotropy, and S1 polarization orientations, which reflect the nearly hexagonal symmetry of brucite's elastic properties at low pressure and the increasingly trigonal nature (threefold c -axis at the center of the pole figure) with increasing pressure.

(~ 15 GPa, 1400°C) is however only about 0.9 wt.% (Demouchy et al., 2005) as temperature has an important affect on solubility. In ringwoodite, water solubility decreases with increasing temperature. In subducting slabs, hydrous wadsleyite and ringwoodite can represent volume fractions of about 50–60%, resulting in the shallower region of the mantle transition zone having a larger water storage potential than the deeper region (Ohtani et al., 2004).

In upper part of the transition zone (410–520 km depth), anhydrous wadsleyite is replaced by hydrous wadsleyite in the hydrated slab. The elastic constants of hydrous wadsleyite have been determined at ambient conditions as a function of water content by Mao et al. (2008a,b). Anhydrous wadsleyite (Zha et al., 1997) has P- and S-wave anisotropies of 15.4% and 16.8%, respectively, whereas hydrous wadsleyite with 1.66 wt.% H_2O has a P-wave and S-wave anisotropies of 16.3% and 16.5%, respectively. Hence, hydration increases V_p anisotropy by 0.9% and decreases V_s anisotropy by 0.3%. Anhydrous wadsleyite has V_p/V_{s1} and V_p/V_{s2} anisotropy values of 22.0% and 19.1%, whereas hydrous wadsleyite has V_p/V_{s1} and V_p/V_{s2} of 20.9% and 20.2%, respectively. For V_p/V_{s1} and V_p/V_{s2} anisotropies, the hydration of wadsleyite decreases V_p/V_{s1} by 0.1% and increases V_p/V_{s2} by 1.1%. Clearly, it is not possible to distinguish between anhydrous wadsleyite and hydrous wadsleyite on the basis of anisotropy, although there is a linear decrease of velocity with water content at room pressure (Mao et al., 2008a). A first-principles study of wadsleyite as function of water content (Tsuchiya and Tsuchiya, 2009) successfully reproduces the experimental elastic results for anhydrous wadsleyite (Zha et al., 1997) and hydrous wadsleyite (Mao et al., 2008a,b) using a Mg vacancy model for the protonation of wadsleyite. Tsuchiya and Tsuchiya (2009) also studied the effect of pressure on hydrous wadsleyite. The pressure derivatives (dC_{ij}/dP) for hydrous wadsleyite are similar to anhydrous derivatives of Zha et al. (1997). At a pressure of 20 GPa, the anhydrous wadsleyite has P- and S-wave anisotropy of 10.1% and 11.9%, whereas hydrous wadsleyite (3.3 wt.% H_2O) has P- and S-wave anisotropy

of 11.3% and 12.8%. At the same pressure, the anhydrous wadsleyite has V_p/V_{s1} and V_p/V_{s2} anisotropies of 13.4% and 9.6%, respectively, whereas hydrous wadsleyite has V_p/V_{s1} and V_p/V_{s2} anisotropies of 14.6% and 11.9%. Hence, hydration of P- and S-wave anisotropies increases by 1.2% and 0.9%, respectively, and for V_p/V_{s1} and V_p/V_{s2} anisotropies increases by 2.2% and 1.6%, respectively. So once again hydration has more effect on velocities than the anisotropy.

In the lower part of the transition zone (520–670 km depth), anhydrous ringwoodite will be replaced by its hydrated counterpart hydrous ringwoodite in the hydrated slab. The elastic constants of hydrous ringwoodite have been measured as a function of pressure to 9 GPa by Jacobsen and Smyth (2006) and to 24 GPa by Wenk et al. (2006). More recently, Mao et al. (2011, 2012) had determined the elastic constants of hydrous ringwoodite to 16 GPa and 673 K. The presence of 1.1 wt.% water lowers the elastic moduli by 5–9%, but does not affect the pressure derivatives. The reduction caused by 1.1 wt.% water is significantly enhanced by high temperature when at high pressure. Hydrous ringwoodite at 16.3 GPa and 673 K has a very low anisotropy, 1.3% for P-waves and 3.0% S-waves. The anisotropy of V_p/V_{s1} and V_p/V_{s2} is slightly stronger at 3.1% and 3.9%, respectively. The pressure sensitivity of the seismic anisotropy of hydrous or hydrated minerals at upper mantle and transition zone pressures is illustrated in Figure 20.

Apart from hydrated phases associated with subduction, there are the phases derived from MORB and sediments (Figure 1). Compared to the pyrolite mantle composition, MORB is chemically enriched in incompatible elements (silicon, aluminum, calcium, and sodium) and depleted in compatible elements like magnesium. At deep mantle temperatures and pressures, MORB transforms to mineral assemblages with high SiO_2 and aluminum content. Mineral assemblages change with pressure and depth at the top of the lower mantle in the pressure range 23–50 GPa (depth range 670–1300 km); the assemblage is composed of the new aluminum phase (NAL), aluminum-rich calcium ferrite structure (Al-CF),

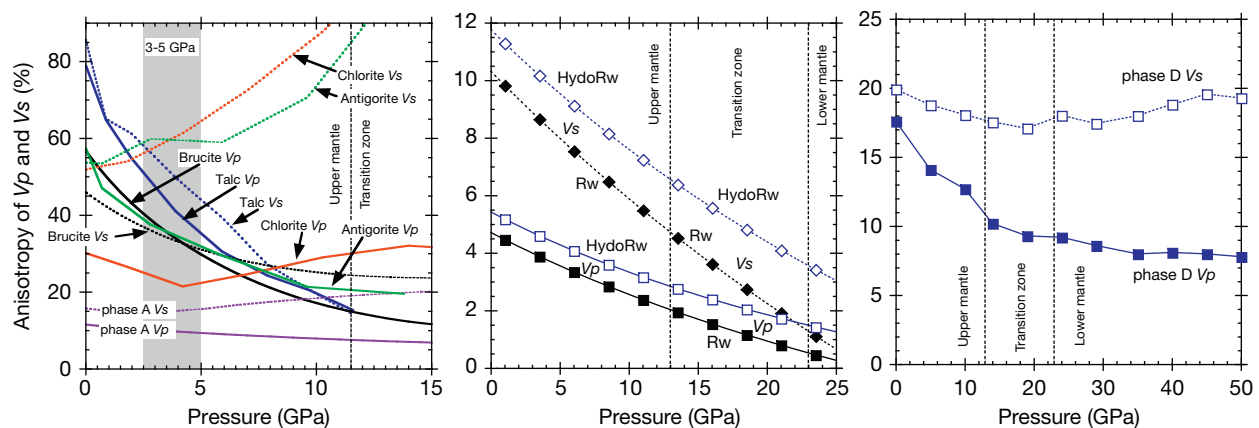


Figure 20 The evolution of seismic anisotropy of hydrous or hydrated minerals in the pressure range of the upper mantle, transition zone, and lower mantle. The pressure range 3–5 GPa is typical of the mantle wedge. In the upper mantle pressure range, the strong pressure sensitivity of brucite, talc, antigorite, and chlorite contrasts with that of the DHMS phase A. Antigorite and chlorite are exceptions as the anisotropy for V_s increases with pressure. Increasing pressure reduces anisotropy with pressure for anhydrous and hydrated ringwoodite in the transition zone. Pressure has a small effect on the V_s anisotropy for DHMS phase D, but increasing pressure decreases V_p anisotropy. See text for discussion and references.

Mg-perovskite, Ca-perovskite, and stishovite that are stable; and of these minerals, NAL, Al-CF, and stishovite are specific to MORB chemistry. Above a pressure of 45–50 GPa (below a depth of 1200 km), NAL (hexagonal, space group $P6_3/m$) is no longer stable due to the increased solubility of aluminum with pressure in the Mg-perovskite (Perrillat et al., 2006; Ricolleau et al., 2010; Sanloup et al., 2013). Stishovite with rutile structure transforms to the CaCl_2 structure of SiO_2 at 55 GPa (depth of about 1300 km) (Andrault et al., 1998), whereas Al-CF (orthorhombic, space group $Pbnm$) is stable to at least 130 GPa (Hirose et al., 2005; Ono et al., 2005a,b). The aluminum-rich calcium titanate structure (Al-CT) (orthorhombic, space group $Cmcm$) mineral is only observed by Ono et al. (2005a,b) at CMB pressure of 143 GPa. Sediments are the other chemical source in subduction zones that can produce minerals like K-hollandite (Irifune et al., 1994).

The elasticity of the relatively low-pressure NAL phase has been studied by Mookherjee et al. (2012) using *ab initio* methods to a pressure of 160 GPa. According to Ricolleau et al. (2010), NAL is only present in the MORB mineral assemblage in the pressure range from 22 to 50 GPa. At 27 GPa, the P- and S-wave anisotropies are 11.3% and 16.0%, respectively. As the NAL phase is hexagonal, the anisotropy has the same elastic symmetry as a transverse isotropic sample. The Al-CF phase has been studied by Tsuchiya (2011), Mookherjee (2011a), and Mookherjee et al. (2012) all using *ab initio* methods. The Al-CF phase has stability over a wide range of pressure in the lower mantle from 22 to 130 GPa (Hirose et al., 2005; Ono et al., 2005a,b; Perrillat et al., 2006; Ricolleau et al., 2010; Sanloup et al., 2013). The orthorhombic symmetry of Al-CF phase results in a more complex velocity distribution than the NAL phase. The elasticity of MgAl_2O_4 CF phase has been calculated by Tsuchiya (2011) and Mookherjee (2011a), the results for the P- and S-wave anisotropies as function of pressure are shown in Figure 21, both P- and S-wave anisotropies decrease with increasing pressure, and the results of these two studies agree very closely. At low-pressure end of the

stability field, P-wave anisotropy is 15.2% and S-wave is 25.0%, and at the high-pressure end of the stability field, 6.5% and 15.3%, respectively. The P- and S-wave anisotropies of the Al-rich calcium titanate structure (Al-CT) at 140 GPa are 11.6% and 28.1%, respectively, near the CMB. So Al-CT has quite high S-wave anisotropy even at extreme pressures.

High-pressure studies on sediments of average continental crust composition between 9 and 24 GPa found that hollandite (now called hollandite I or lingunite) represents ~30% by volume of the high-pressure assemblage (Irifune et al., 1994), indicating the importance of the hollandite I phase for subducted sediments. Under ambient conditions, hollandite I has tetragonal symmetry $I4/m$. Using high-pressure *in situ* RXD techniques up to 32 GPa (Ferroir et al., 2006; Sueda et al., 2004) showed that hollandite I undergoes a phase transition from the tetragonal to a monoclinic hollandite II phase with $I2/m$ symmetry at 20 GPa at room temperature. Phase equilibrium studies on the system KAlSi_3O_8 – $\text{NaAlSi}_3\text{O}_8$ by Liu (2006) show that hollandite I is stable up to 18 GPa and 2200 °C and hollandite II is stable up to 25 GPa and 2000 °C. Hollandite I and hollandite II can be present in the transition zone and the upper part of the lower mantle and perhaps to greater depths. An elasticity study using *ab initio* methods by Mookherjee and Steinle-Neumann (2009b) reports the P-wave anisotropy for hollandite I as about 26% at zero pressure, which decreases at the transition pressure of about 30 GPa to 22%. The P-wave anisotropy of hollandite II at the transition pressure is 20%, and this slowly decreases to 12% at 100 GPa. The S-wave anisotropy of hollandite I is 42% at zero pressure, but rises sharply to 70% at the 30 GPa. Hollandite II at the transition pressure has V_s anisotropy of 30%, which slowly decreases with increasing pressure to 22% at 100 GPa (Figure 21). Hollandite I and hollandite II have very high S-wave anisotropies compared to other minerals in the transition zone and lower mantle. Mussi et al. (2010) had shown that hollandite I deforms plastically at transition zone temperatures and pressures and predicted CPO that would

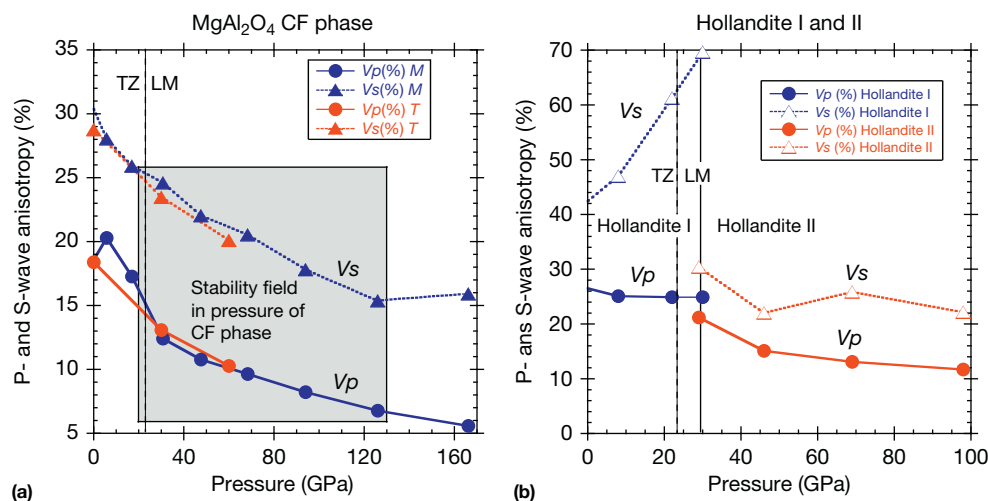


Figure 21 The effect of pressure on the seismic anisotropy of anhydrous phases, CF phase and hollandite I and hollandite II. The CF phase (T =Tsuchiya, 2011; M =Mookherjee, 2011a) shows a typical decrease of anisotropy of V_p and V_s with increasing pressure seen in minerals like talc and brucite. Hollandite I (Mookherjee and Steinle-Neumann, 2009b) is atypical with increasing V_s anisotropy with pressure, like antigorite and chlorite. In hollandite II, the V_p and V_s anisotropies decrease slightly with pressure.

result in seismic anisotropy very similar to stishovite (Cordier et al., 2004a), as both minerals have the same rutile structure. Aggregates of hollandite I are predicted to have P- and S-wave anisotropies of 12.8% and 15.1%, compared to stishovite aggregate with 8.9% and 7.1% at the same pressure of 17 GPa, which corresponds to a depth of about 500 km.

Subducted MORB will produce SiO_2 phase such as coesite, stishovite, and the poststishovite high-pressure phases. Stishovite is stable from 9 to 24 GPa in the experiments of Irifune et al. (1994) and can be stable until 55 GPa (Andrault et al., 1998). In experiments on sediments by Irifune et al. (1994), stishovite has a volume fraction between 20% and 40%, whereas in transform MORB, stishovite has volume fractions of 15–20% (Ricolleau et al., 2010). Using *ab initio* methods Karki et al. (1997a,b,c) has given the elastic constants of SiO_2 polymorphs, and recently, full set experimental values to 12 GPa have been measured by Jiang et al. (2009), and these are in close agreement with the predictions of Karki et al. (1997a,b,c). The transformation pressure and temperature of stishovite to CaCl_2 -type SiO_2 phase have been given by *ab initio* methods by Tsuchiya et al. (2004). From the anisotropy point of view, stishovite starts to become exceptional at about 670 km discontinuity when the S-wave anisotropy is greater than 50% (Figure 22). From 670 km discontinuity to the eventual transformation to CaCl_2 -type SiO_2 at about 1200 km depth, the S-wave anisotropy sharply increases to an exceptional value of about 150% near the transition. In parallel with the evolution of the S-wave anisotropy, the V_p/V_s2 ratio also reaches unprecedented value of 10 (Figure B). Stishovite deforms plastically at high temperature and pressure (Cordier et al., 2004a,b) and is expected to form CPO as predicted by polycrystalline modeling, and a strong anisotropy is expected in real mantle samples. Kawakatsu and Niu (1994) and Vinnik et al. (2001) had observed seismic reflectivity in the lower mantle, which may be explained by the SiO_2 phase transformation at around 1100–1200 km.

A wide range of temperature and pressure associated with several chemical sources represented by the pyrolite mantle, MORB, and sediments create a complex pattern of minerals with depth in subduction zones. The subduction zones are compared to the extensive volumes involved with convective mantle and are quite narrow and restricted volumes. The thermomechanical constraints of a subduction zone are a number of minerals that are very anisotropic: antigorite, talc, chlorite, brucite, hollandite I, Al-CF phase, and stishovite. In almost all minerals, the P-wave anisotropy decreases with increasing pressure. The very anisotropic minerals fall into two groups: (a) a group where the S-wave anisotropy decreases with pressure that includes talc, brucite (Figure 20), and Al-CF phase (Figure 21) and (b) a group where the S-wave anisotropy increases with pressure that includes antigorite, chlorite, hollandite I, and stishovite (Figures 20, 21, and 22, respectively).

2.20.2.6.5 Inner core

Unlike the mantle, the Earth's inner core is composed primarily of iron, with about 5 wt.% nickel and very small amounts of other siderophile elements such as chromium, manganese, phosphorus, and cobalt and some light elements such as oxygen, sulfur, and silicon. The stable structure of iron at ambient conditions is body-centered cubic (bcc); when the pressure is increased above 15 GPa, iron transforms to an hcp structure called the ϵ -phase; and at the high pressure and temperature, iron most likely remains hcp; however, there have been experimental observations of a double hexagonal close-packed structure (dhcp) (Saxena et al., 1996) and a distorted hcp structure with orthorhombic symmetry (Andrault et al., 1997). Atomic modeling at high pressure and high temperature suggests that the hcp structure is still stable at temperatures above 3500 K in pure iron (Vočadlo et al., 2003a), although the energy differences between the hcp and the bcc structures are very small and the authors speculate that

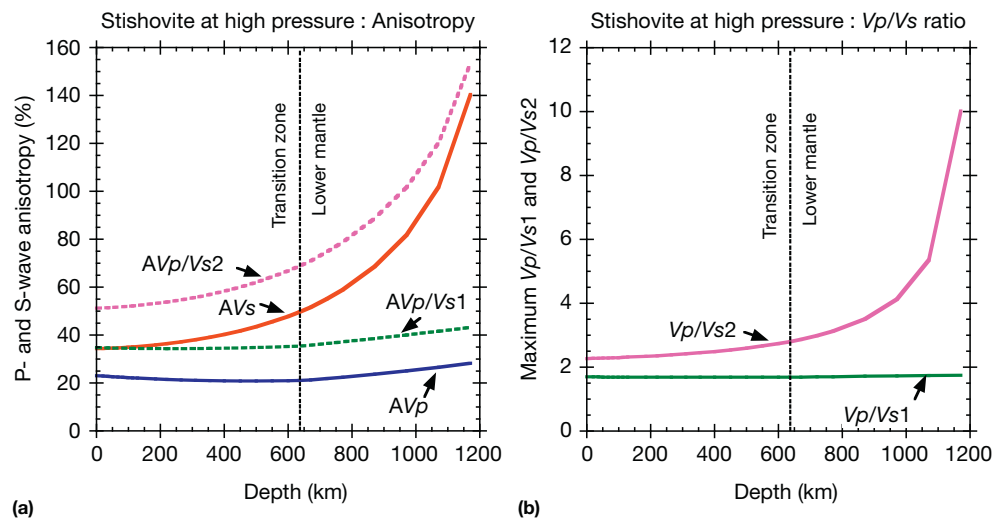


Figure 22 The effect of depth on the seismic anisotropy of anhydrous stishovite SiO_2 using the *ab initio* predicted elastic constants of Karki et al. (1997a,b,c). The rutile-structured stishovite reaches exceptionally high V_s anisotropy (150%) near phase transition to the CaCl_2 structured form of SiO_2 at about 1100 km depth. In contrast, V_p anisotropy increases with depth to about 30%. The parameters associated with $Vs2$, such as the ratio of $V_p/Vs2$ and anisotropy of $V_p/Vs2$, both reach exceptional values near the phase transition.

the bcc structure may be stabilized by the presence of light elements. A suggestion is echoed by the seismic study of Beghein and Trampert (2003). To make a quantitative anisotropic seismic model to compare with observations, one needs either velocity measurements or the elastic constants of single-crystal hcp iron at the conditions of the inner core. The measurement or first-principles calculation of the elastic constants of iron is a major challenge for mineral physics. The conditions of the inner core are extreme with pressures from 325 to 360 GPa and temperatures from 5300 to 5500 K. To date, experimental measurements have been using DACs to achieve the high pressures on polycrystalline hcp iron. IXS has been used to measure V_p at room temperature and high pressure up to 112 GPa and temperatures up to 1100 K (Antonangeli et al., 2004, 2010, 2012; Fiquet et al., 2001), and the anisotropy of V_p has been characterized in two directions up to 112 GPa (Antonangeli et al., 2004). V_p has been determined at simultaneous high pressure and temperature up to 300 GPa and up to 1200 K from x-ray Debye–Waller temperature factors (Dubrovinsky et al., 2001) and up to 73 GPa and 1700 K using IXS by Lin et al. (2005). x-Ray radial diffraction (XRD) has been used to measure the elastic constants of polycrystalline iron with simultaneous measurement of the CPO at room temperature and pressures up to 211 GPa (Singh et al., 1998; Mao et al., 1998, with corrections 1999; Merkel et al., 2005), which is still well below inner core pressures. However, as mentioned before, the high nonhydrostatic stress present in DACs has exceeded the plastic yield stress in some experiments and produced plastic strain, which violates the elastic stress analysis used to determine the elastic parameters (Antonangeli et al., 2006; Mao et al., 2008a,b,c; Merkel et al., 2006a,b, 2009). The experimental V_p data used to describe the anisotropy of textured polycrystalline samples are shown in Figure 23. The texture or CPO of the iron is induced by the compression in DAC with an axial symmetry. The original experiments of H.K. Mao et al. (1998) show the characteristic bell-shaped V_p curve with peak velocity near 45° from the compression direction, which is also the symmetry axis (Figure 23(a)). Note also that even the IXS data points of Antonangeli et al. (2004) have similar symmetry to the data

of Mao et al. (1998). Recently, a new combined method was introduced by Mao et al. (2008a,b,c) to avoid problems in DAC, which uses IXS and the EOS. In the 2008 paper, they reproduced the old method with bell-shaped curve and introduced the new method, which has the maximum V_p nearer the symmetry axis (Figure 23(b)). More recent work using IXS uses gas-loaded DAC to avoid or reduce nonhydrostatic stresses (Antonangeli et al., 2010, 2012), but has not studied anisotropy.

In order to simulate the *in situ* conditions, the static (0 K) elastic constants have been calculated at inner core pressures (Stixrude and Cohen, 1995). The calculated elastic constants predict maximum P-wave velocity parallel to the c -axis, and the difference in velocity between the c - and a -axes is quite small (Figure 23(a)). The anisotropy of the calculated elastic constants being quite low required that the CPO is very strong, and it was even suggested that inner core could be a single crystal of hcp iron to be compatible with the seismic observations and that c -axis is aligned with the Earth's rotation axis. The first attempt to introduce temperature into first-principles methods for iron by Laio et al. (2000) produced estimates of the isotropic bulk and shear modulus at inner core conditions (325 GPa and 5400 K) and single-crystal elastic constants at conditions comparable with the experimental study of Mao et al. (1998) (210 GPa and 300 K). The next study to simulate inner core temperatures (4000–6000 K) and pressures by Steinle-Neumann et al. (2001) produced two unexpected results: firstly the increase of the unit cell axial c/a ratios by a large amount (10%) with increasing temperature and secondly the migration of the P-wave maximum velocity to the basal plane and normal to the c -axis at high temperature. These new high-temperature results required a radical change in the seismic anisotropy model with one-third of c -axes being aligned normal to the Earth's rotation axis (Steinle-Neumann et al., 2001) giving an excellent agreement with travel time differences. However, more recent calculations (Gannarelli et al., 2003, 2005; Sha and Cohen, 2006) have failed to reproduce the large change in c/a axial ratios with temperature, which casts some doubt on the elastic constants of Steinle-Neumann et al. at high temperature. It should be said that high-temperature

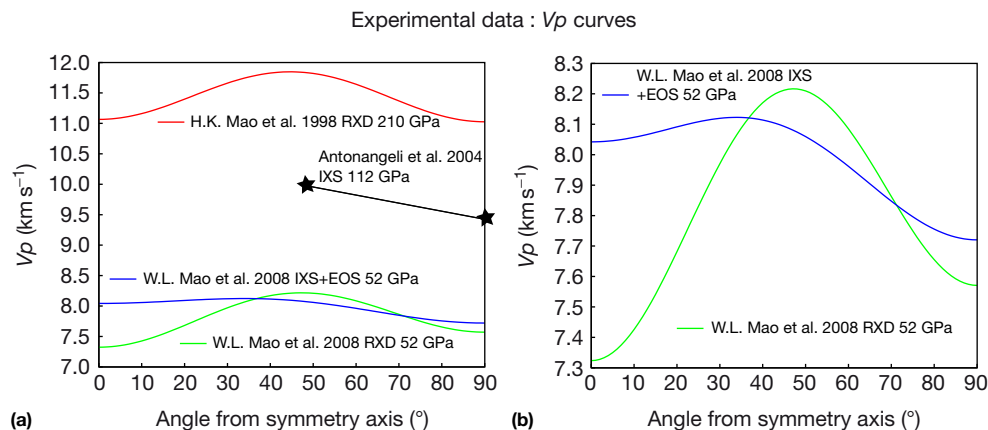


Figure 23 The seismic velocities at ambient temperature in single-crystal pure hexagonal close-packed ϵ -phase iron calculated from the experimentally determined elastic constants of Mao et al. (1998, with correction 1999) and Mao et al. (2008a,b,c) or measured velocity in the case of Antonangeli et al. (2004). RXD, radial x-ray diffraction; IXS, x-ray scattering; EOS, equation of state (see text for discussion).

first-principles calculations represent frontier science in this area. What is perhaps even more troublesome is that there is very poor agreement, or perhaps one should say total disagreement, between experimental results and first principles for P- and S-wave velocity distribution in single-crystal hcp iron at low temperature and high pressure where methods are considered to be well established. The experimental techniques can be criticized as mentioned before. However, differences can be seen in the magnitude of the anisotropy and the position of the minimum velocity, minimum at 50° from the c -axis (Steinle-Neumann et al., 2001; Stixrude and Cohen, 1995) or at 90° (Laio et al., 2000; Vočadlo et al., 2003b). In recent years, a new consistency has appeared in the *ab initio* models for the inner core. In Figure 24, we have selected some original milestones like the Mao et al. (1998) experimental curve with bell shape, which today is considered an experimental artifact. The first OK *ab initio* model of hcp iron at core pressures by Stixrude and Cohen (1995) and an early finite temperature *ab initio* model by Steinle-Neumann et al. (2001) show to illustrate the degree of disagreement between these pioneering studies. All the other studies are recent from 2010 to 2013 all at inner temperatures and pressures, all for hcp iron, a part from one for bcc iron from Mattesini et al. (2010). Using the weak cylindrical seismic model for hemispherical inner core anisotropy of Lythgoe et al. (2014), we can compare with travel time residuals ($\delta t/t$) predicted by *ab initio* elasticity models of iron. From Figure 24, we can see that seismic anisotropy between the hemispheres is very different, and single model will not explain both hemispheres. Several models are in agreement with stronger anisotropy of the western hemisphere (hcp Stixrude and Cohen, 1995; hcp and bcc from Mattesini et al., 2010), corresponding to V_p anisotropies between 4.1% and 6.3%. Two models are also in agreement with the weaker seismic anisotropy observations for eastern hemisphere, notably (hcp, Stixrude and Cohen, 1995; hcp, Sha and Cohen, 2010)

corresponding to V_p anisotropies between 2.4% and 4.1%. All the *ab initio* models are present as transverse isotropic symmetry with the symmetry axis parallels to the Earth's rotation axis. In the hcp iron, which has hexagonal symmetry, this requires that c -axis of the single crystal to be parallel to the rotation axis. In the case of bcc iron, the direction of maximum V_p is the $[111]$ direction, and all the crystals in the model aggregate are rotated about $[111]$ to produce transverse isotropic symmetry. So for hcp iron, the *ab initio* curves represent the maximum possible single-crystal anisotropy, and in the western hemisphere, there are seismic observations with anisotropy stronger than perfectly aligned c -axis of the hcp iron single crystals or bcc iron $[111]$ axis is perfectly aligned. The bcc model of Mattesini et al. (2010) produces the strongest V_p anisotropy at 6.3%, but it is less strong than the seismic western hemisphere measurements of Lythgoe et al. (2014) at the layer three of their model (Figure 2), which corresponds to less than 550 km from the center of the Earth. In addition, it is interesting to note that recent experimental studies at 340 GPa and 4700 K favor the hcp rather than bcc as the stable structure of iron in the inner core (Tateno et al., 2012). It is not clear what mechanism would produce such perfect alignment; it seems unlikely to be caused by plasticity as this results in non-perfect statistical alignment, unless there is more anisotropic iron crystal structure than presently known in the inner core or the extreme conditions near the center of the Earth. The processes related to melting and crystallization has been recently invoked by several studies of hemispherical nature of the inner core (Alboussière et al., 2010; Aubert et al., 2011; Deguen and Cardin, 2009; Gubbins et al., 2011; Monnereau et al., 2010). It is possible that other compositions of iron-related phases might have greater anisotropy than pure iron and currently known alloys, for example, orthorhombic cementite (Fe_3C), which has V_p anisotropy of 10.3% at inner core pressures (Mookherjee, 2011b).

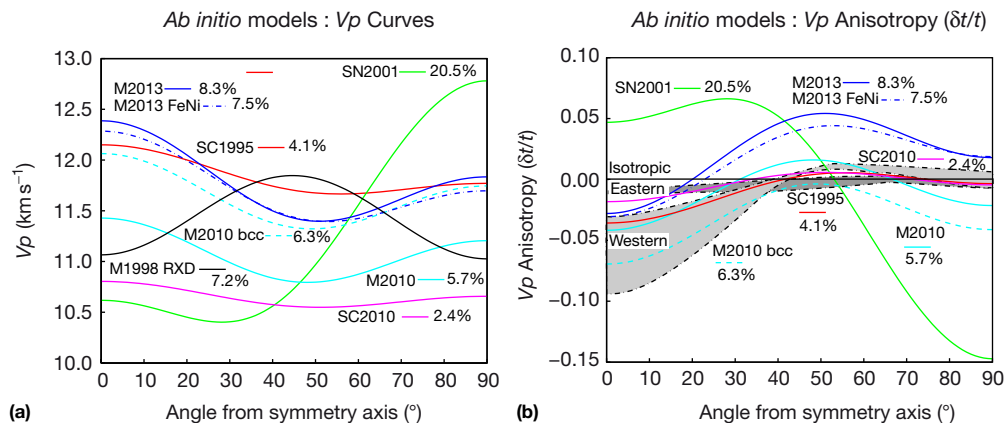


Figure 24 (a) The seismic velocities at 0 K or high temperature in single-crystal hexagonal ϵ -phase iron calculated from the *ab initio* determined elastic constants at inner core pressures, with experimental V_p of Mao et al. (1998, 1999) at 210 GPa at room temperature for reference. (b) The predicted P-wave anisotropy for the inner core using the *ab initio* elastic constants, with the seismic results of Lythgoe et al. (2014) for eastern (dark gray region with black dashed line outlines) and western (light gray) hemispheres. Numbers with percent sign are the V_p -wave anisotropies for each *ab initio* model and the experimental data of Mao et al. (1998, 1999). All models are for pure crystal hexagonal close-packed hexagonal ϵ -phase iron, except where otherwise specified. Bcc stands for pure body-centered cubic α -phase iron. SC1995 = Stixrude and Cohen (1995) at 0 K, SN2001 = Steinle-Neumann et al. (2001) at 6000 K, SC2010 = Sha and Cohen (2010) at 6000 K, M2010 = Mattesini et al. (2010) at 6000 K, M2010 bcc has the same authors and temperature with bcc structure, M2013 = Martorell et al. (2013) at 5500 K, and M2013 FeNi has the same authors and temperature with a composition of 87.5% Fe 12.5% Ni. See text for discussion.

From this brief survey of recent results in this field, it is clear there is still much to do to unravel the meaning of seismic anisotropy of the inner core and physics of iron at high pressure and temperature in particular. Although the stability of hcp iron at inner core conditions has been questioned from time to time on experimental or theoretical grounds, which the inner core may not be pure iron (e.g., Poirier, 1994), the major problem at the present time is to get agreement between theory and experiment at the same physical conditions. Interpretation of the mechanisms responsible for inner core seismic anisotropy is out of the question without a reliable estimate of elastic constants of pure iron and its alloys; nowhere in the Earth is Francis Birch's 'high-pressure language' (positive proof=vague suggestion, Birch, 1952) more appropriate.

2.20.3 Rock Physics

2.20.3.1 Introduction

In this section, I will illustrate the contribution of CPO to seismic anisotropy in the deep Earth with cases of olivine and the role of melt. The CPO in rocks of upper mantle origin is now well established (e.g., Mainprice et al., 2000; Mercier, 1985; Nicolas and Christensen, 1987) as direct samples are readily available from the first 50 km or so, and xenoliths provide further sampling down to depths of about 220 km. Ben and Mainprice (1998) created a database of olivine CPO patterns from a variety of the upper mantle geodynamic environments (ophiolites, subduction zones, and kimberlites) with a range of microstructures. However, for the deeper mantle (e.g., Wenk et al., 2004) and inner core (e.g., Merkel et al., 2005), we had to rely traditionally on high-pressure and high-temperature experiments to characterize the CPO at extreme conditions. In recent years, the introduction of various types of polycrystalline plasticity models to stimulate CPO development for complex strain paths has allowed a high degree of forward modeling using either slip systems determined from studying experimentally deformed samples using transmission electron microscopy (e.g., wadsleyite – Thurel et al., 2003; ringwoodite – Karato et al., 1998), RXD peak broadening analysis for electron radiation sensitive minerals (e.g., Mg-perovskite – Cordier et al., 2004b), or predicted systems from atomic-scale modeling of dislocations (e.g., olivine, Durinck et al., 2005a,b and ringwoodite, Carrez et al., 2006). The polycrystalline plasticity modeling has allowed forward modeling of upper mantle (e.g., Blackman et al., 1996; Chastel et al., 1993; Tommasi, 1998), transition zone (e.g., Tommasi et al., 2004), lower mantle (e.g., Mainprice et al., 2008a,b; Wenk et al., 2006), D'' layer (e.g., Merkel et al., 2006a), and the inner core (e.g., Jeanloz and Wenk, 1988; Wenk et al., 2000).

2.20.3.2 Olivine the Most-Studied Mineral: State-of-the-Art-Temperature, Pressure, Water, and Melt

Until the papers by Jung and Karato (2001), Katayama et al. (2004), and Katayama and Karato (2006) were published, the perception of olivine-dominated flow in the upper mantle was quite simple with [100] {0kl} slip being universally accepted as the mechanism responsible for plastic flow and

the related seismic anisotropy (e.g., Mainprice et al., 2000). The experimental deformation of olivine in hydrous conditions at 2 GPa pressure and high temperature by Karato and coworkers produced a new type of olivine CPO developed at low stress with [001] parallel to the shear direction and (100) in the shear plane, which they called C type, which is associated with high water content. They introduced a new olivine CPO classification that illustrated the role of stress and water content as the controlling factors for the development of five CPO types (A, B, C, D, and E) (Figure 25). The five CPO types are assumed to represent the dominant slip system activity on $A \equiv [100](010)$, $B \equiv [001](010)$, $C \equiv [001](100)$, $D \equiv [100]\{0kl\}$, and $E \equiv [100](001)$. I have taken the Ben and Mainprice (1998) olivine CPO database with 110 samples and estimated the percentages for each CPO type and added an additional class called AG type (or axial b -[010] girdle by Tommasi et al., 2000), which is quite common in naturally deformed samples, particularly in samples that have been associated with melt-rock interaction (e.g., Higgie and Tommasi, 2012). The CPO types in percentage of the database are A type (49.5%), D type (23.8%), AG type (10.1%), E type (7.3%), B type (7.3%), and C type (1.8%). It is clear that CPO associated with [100] direction slip (A, AG, D, and E types) represents 90.8% of the database and therefore only 9.2% is associated with [001] direction slip (B and C types). Natural examples of all CPO types taken from the database are shown in Figure 26, with the corresponding seismic properties in Figure 27. There are only one unambiguous C-type sample and another with transitional CPO between B and C types. The database contains samples from paleo-mid-ocean ridges (e.g., Oman ophiolite), the circum-Pacific subduction zones (e.g., Philippines, New Caledonia, Canada), and subcontinental mantle (e.g., kimberlite xenoliths from South Africa). There have been some recent reports of the new olivine B-type CPO (e.g., Mizukami et al., 2004) associated with high water content, and other B and C types from ultrahigh-pressure (UHP) rocks (e.g., Xu et al., 2006) have relatively low water contents. It is instructive to look at the solubility of water in olivine to understand the potential importance of the C-type CPO. In Figure 28, the experimentally determined solubility of water in nominally anhydrous upper mantle silicates (olivine, cpw, opx, and garnet) in the presence of free water is shown over the upper mantle pressure range. The values given in the review by Bolfan-Casanova (2005) are in H₂O ppm wt. using the calibration of Bell et al. (2003), so the values of Karato et al. in H/10⁶ Si using the infrared calibration of Paterson (1982) have to be multiplied by 0.22 to obtain H₂O ppm wt. If free water is available, then olivine can incorporate, especially below 70 km depth, many times the concentration necessary for C-type CPO to develop according to the results of Karato and coworkers.

Why is it that the C-type CPO is relatively rare? It is certain that deforming olivine moving slowly towards the surface will lose its water due to the rapid diffusion of hydrogen. For example, even xenoliths transported to the surface in a matter of hours lose a significant fraction of their initial concentration (Demouchy et al., 2005). Hence, it is very plausible that in the shallow mantle (less than about 70 km depth), the C type will not develop because the solubility of water is too low in olivine at equilibrium conditions and that 'wet' olivine upwelling

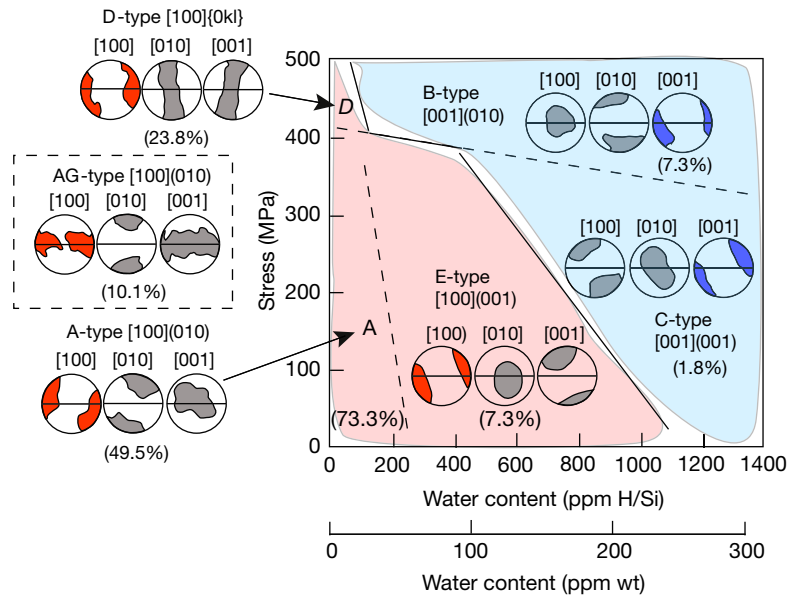


Figure 25 The classification of olivine CPO originally proposed by Jung and Karato (2001) and Karato et al. (2008) as a function of stress and water content. The water content scale in ppm H/Si is that originally used by Jung and Karato. The water content scale in ppm wt is more recent calibration used by Bolfan-Casanova (2005). The numbers in brackets are the percentage of samples with the fabric types found in the database of Ben Ismail and Mainprice (1998). On the pole figure, red indicates [100] parallel to lineation and blue indicates [001] parallel to lineation in samples from the olivine CPO database.

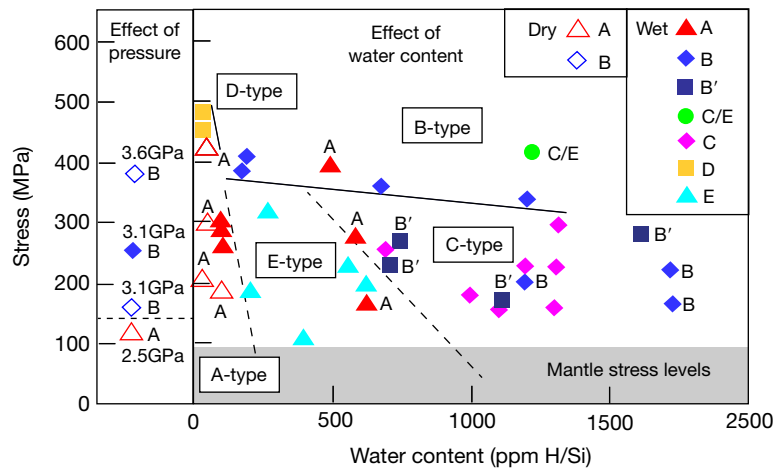


Figure 26 In the left-hand panel the experimental data of Ohuchi et al. (2012) on the effect of water and stress for the development of olivine CPO. In the right-hand panel the experimental data of Jung et al. (2008) on the effect of pressure and stress on the development of dry olivine CPO. The CPO fields proposed by Jung and Karato (2001) and Karato et al. (2008) as a function of stress and water content are marked with black solid or dashed lines. In the right-hand panel the symbols with no letter next to them come from Karato et al. (2008) and symbols with a letter come from Ohuchi et al. (2012). CPO types C/E and B' are transitional CPO defined by Ohuchi et al. (2012). Open symbol represents dry samples or no water detected. In the left-hand panel the pressure is indicated in GPa next to each symbol. See text for discussion.

from greater depths and moving towards the surface by slow geodynamic processes will lose their excess water by hydrogen diffusion. In addition, any 'wet' olivine coming into contact with basalt melt will tend to 'dehydrate' as the solubility of water in the melt phase is hundreds to thousands of times greater than olivine (e.g., Hirth and Kohlstedt, 1996). The melting will occur in upwelling 'wet' peridotites at a well-defined depth when the solidus is exceeded and the volume fraction of melt produced is controlled by the amount of water

present. Karato and Jung (1998) estimated that melting is initiated at about 160 km in the normal mid-ocean ridge source regions and at greater depth of 250 km in back-arc-type MORB with the production of 0.25–1.00% melt, respectively. Given the small melt fraction, the water content of olivine is unlikely to be greatly reduced. As more significant melting will of course occur when the 'dry' solidus is exceeded with 0.3% melt per kilometer melting at about 70 km, then 3% or more percent melt is quickly produced and the water

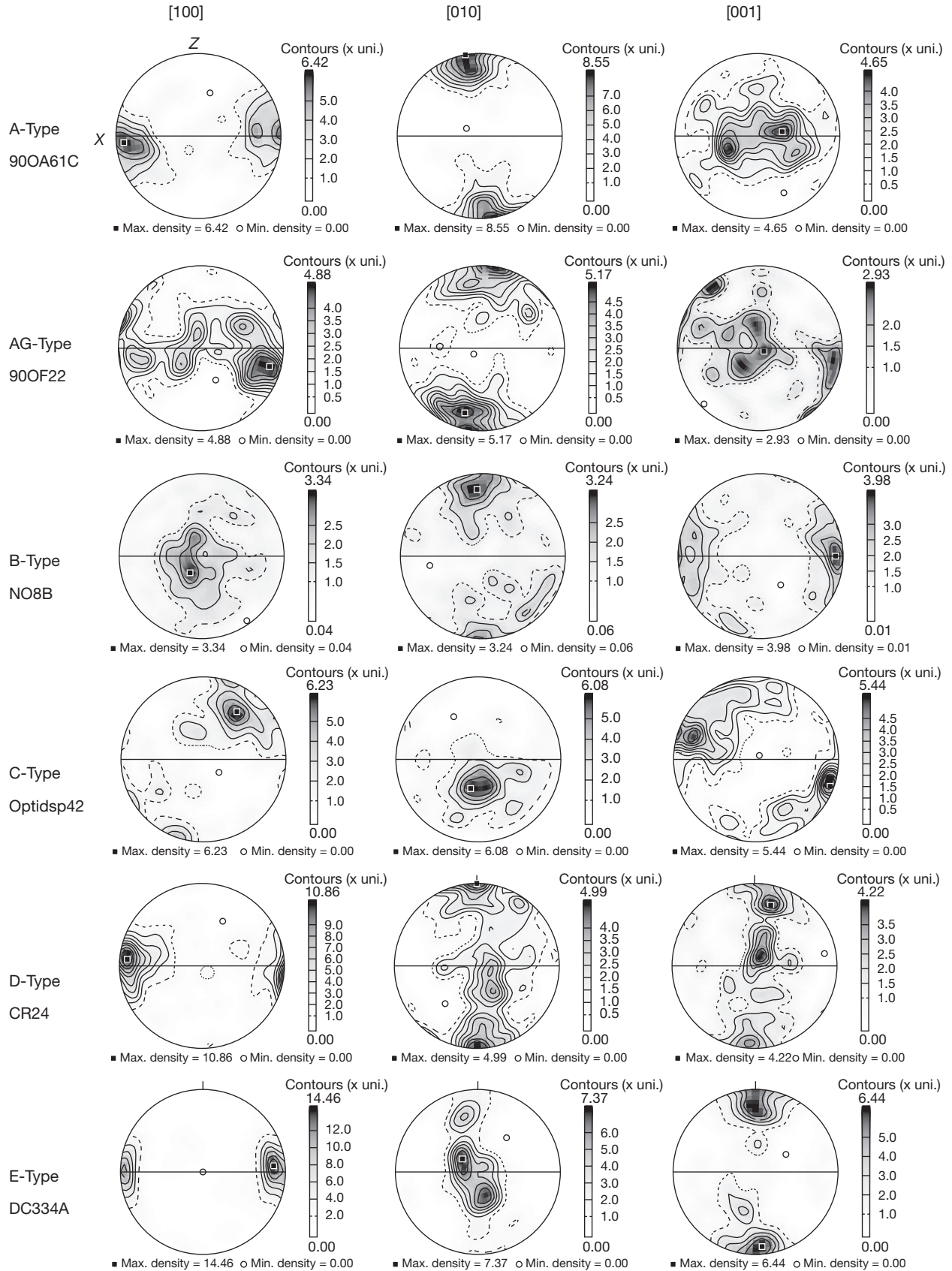


Figure 27 Natural examples of olivine CPO types from the Ben Ismail and Mainprice (1998) database, except the B-type sample NO8B from K. Michibayashi (personal communication, 2006). X marks the lineation; the horizontal line is the foliation plane. Contours given in times uniform.

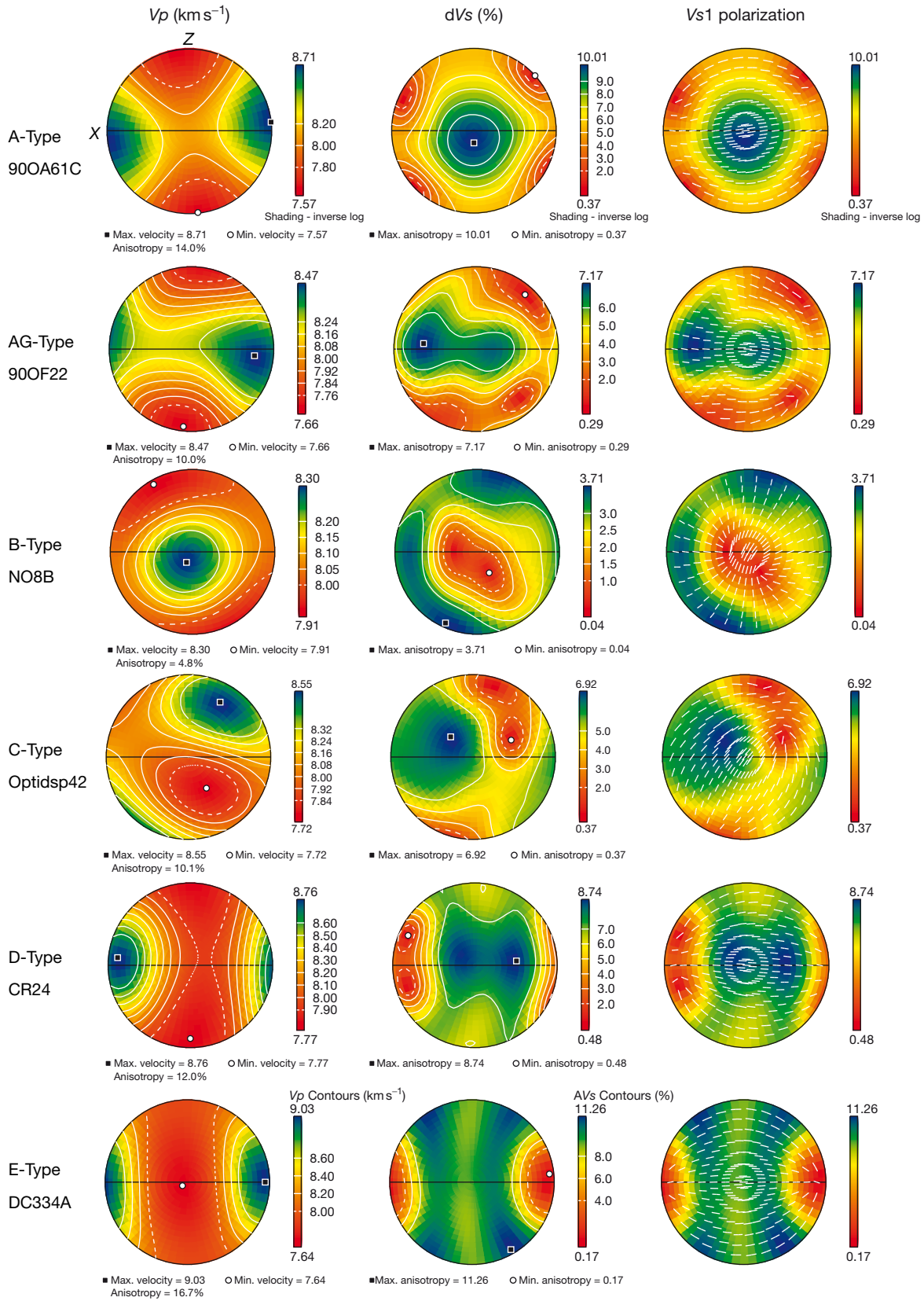


Figure 28 Anisotropic seismic properties of olivine at 1000°C and 3 GPa with CPO of the samples in figure 27. X marks the lineation, the horizontal line is the foliation plane.

content of olivine will be greatly reduced. So the action of reduced solubility and selective partitioning of water into the melt phase are likely to make the first 70 km of oceanic mantle olivine very dry. The other region where water is certainly present is in subduction zones, where relatively water-rich sediments, oceanic crust, and partly hydrated oceanic lithosphere will add to the hydrous budget of the descending slab. Partial melting is confined in the mantle wedge to the hottest regions, where the temperatures approach the undisturbed asthenospheric conditions at 45–70 km depth, and 5–25 wt. % melt will be produced by a lherzolitic source (Ulmer, 2001). Hence, even in the mantle wedge, the presence of large volume fractions of melt is likely to reduce the water content of olivine to low levels, possibly below the threshold of the C-type CPO, for depths shallower than 70 km.

Is water the only reason controlling the development of the C-type fabric or [001] direction slip in general? The development of slip in the [001] direction on (010) and (100) planes at high stresses in olivine has been known experimentally since transmission electron microscopy study of Phakey et al. (1972). More recently, Couvy et al. (2004) had produced B- and C-type CPO in forsterite at very high pressure (11 GPa) using nominally dry starting materials. However, as pointed out by Karato (2006), the postmortem infrared spectrophotometry of the deformed samples revealed the presence of water, presumably due to the dehydration of sample assembly at high pressure. However, concentration of water in the forsterite increases linearly with time at high pressure, whereas the CPO is acquired at the beginning of the experiment in the stress-relaxation tests conducted by Couvy et al. (2004), so it is by no means certain that significant water was present at the beginning of the experiment. Mainprice et al. (2005) suggested it was pressure that was the controlling variable, partly inspired by recent atomic modeling of dislocations in forsterite (Durinck et al., 2005b), that shows the energy barrier for [100] direction slip increases with hydrostatic pressure, whereas for [001], it is constant, which could explain the transition from [100] to [001] with pressure. More recent experiments by Jung et al. (2009) on dry olivine at pressures of 2.1–3.6 GPa report a transition from A-type CPO to B-type CPO with increasing pressure at about 3.1 GPa. Ohuchi et al. (2011) also working on dry olivine samples found the transition pressure from A type to B type is 7.1 GPa. Axial compression experiments using two single crystals of dry San Carlos olivine in series, one favorably oriented for a-direction slip and other for c-slip, find that faster c-slip occurs above 8 GPa (Raterron et al., 2007, 2009). New experiments of Ohuchi et al. (2012) on the deformation of olivine samples in the presence of water show much more complex distribution of CPO types (Figure 29) than reported by Karato et al. (2008). In Figure 29, A types are found with water contents over 500 ppm H/Si, B types are found at lower stress and very high water contents, and no definitive C types are reported by Ohuchi et al. (2012). It appears that both pressure and water content play a role in controlling CPO types, but the experimental scatter is now considerable (Figure 29) and exact relation to water content and pressure needs further calibration.

If we are to accept the experimental results of Karato et al. (2008), what are the seismic consequences of the recent discovery of C-type CPO in experiments in hydrous conditions?

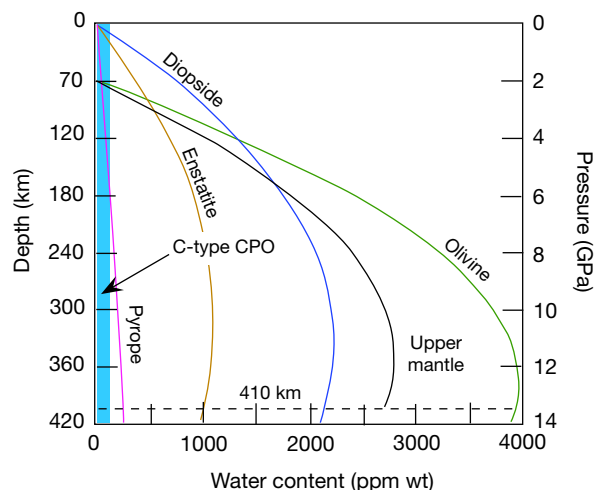


Figure 29 The variation in the water content of upper mantle silicates in the presence of free water from Bolfan-Casanova (2005). The water content of the experimentally produced C-type CPO by Jung and Karato is indicated by the light blue region.

The classic view of mantle flow dominated by with [100] {0kl} slip is not challenged by this new discovery as most of the upper mantle will be dry and at low stress. The CPO associated with [100] slip, which is 90.8% of the Ben Ismail and Mainprice (1998) database, produces seismic azimuthal anisotropy for horizontal flow with maximum V_p , polarization of the fastest S-wave parallel to the flow direction, and $V_{SH} > V_{SV}$. The seismic properties of all the CPO types are shown in Figure 27. It remains to apply the C-, B-, and possibly E-type fabrics to hydrated section of the upper mantle. Katayama and Karato (2006) proposed the mantle wedge in subduction zones is a region where the new CPO types are likely to occur, with the B-type CPO occurring in the low-temperature (high stress and wet) subduction where an old plate is subducted (e.g., NE Japan). The B-type fabric would result anisotropy parallel normal to plate motion (i.e., parallel to the trench). In the back-arc, the A-type (or E-type reported by Michibayashi et al., 2006 in the back-arc region of NE Japan) fabric is likely dominant because water content is significantly reduced in this region due to the generation of island arc magma. Changes in the dominant type of olivine fabric can result in complex seismic anisotropy, in which the fast shear wave polarization direction is parallel to the trench in the forearc but is normal to it in the back-arc (e.g., Kneller et al., 2005). In higher-temperature subduction zones (e.g., NW America, Cascades), the C-type CPO will develop in the mantle wedge (low stress and wet) giving rise to anisotropy parallel to plate motion (i.e., normal to the trench). Although these models are attractive, trench-parallel flow was first described by Russo and Silver (1994) for flow beneath the Nazca Plate, where there is a considerable path length of anisotropic mantle to generate the observed differential arrival time of the S-waves. On the other hand, a well-exposed peridotite body analogue of arc-parallel flow of in south central Alaska reveals horizontal stretching lineations, and olivine [100] slip directions are sub-parallel to the Talkeetna arc for over 200 km, clearly indicating that mantle flow was parallel to the arc axis (Mehl et al., 2003).

The measured CPO of olivine shows that the E-type fabric is dominant along the Talkeetna arc; in this case, foliation is parallel to the Moho suggesting arc-parallel shear with a horizontal flow plane. Tommasi et al. (2006) also reported the E-type fabric with trench-parallel tectonic context in a highly depleted peridotite massif from the Canadian Cordillera in dunites associated with high degrees of melting and hence probably dry, whereas harzburgites have an A-type fabric. In limiting the path length to the region of no melting, in coldest part of the mantle wedge, above the plate, you are also constraining the vertical thickness to about 45–70 km depth, if one accepts the arguments for melting (Ulmer, 2001). For NE Japan, the volcanic front is about 70 km above the top of the slab defined by the hypocenter distribution of intermediate-depth earthquakes (Nakajima and Hasegawa, 2005, their Figure 1), and typical S-wave delay times are 0.17 s (maximum 0.33 s, minimum 0.07 s). The delay times from local slab sources are close to the minimum of 0.07 s for trench-parallel fast S-wave polarizations to the east of the volcanic front (i.e., above the coldest part of the mantle wedge) and are over 0.20 s for the trench normal values (i.e., the back-arc side). Are these CPOs capable of producing a recordable seismic anisotropy over such a short path length? The vertical S-wave anisotropy can be estimated from the delay time given by Nakajima and Hasegawa (2005) (e.g., 0.17 s), the vertical path length (e.g., 70 km), and the average S-wave velocity (e.g., 4.46 km s^{-1}) to give a 1.1% S-wave anisotropy, which is less than maximum S-wave anisotropy of 1.7% given for a B-type CPO in a vertical direction given by Katayama and Karato (2006) for horizontal flow, so B-type CPO is compatible with seismic delay time, even if we allow some complexity in the flow pattern. The case for C type in the high-temperature subduction zones is more difficult to test, as the S-wave polarization pattern will be the same for C and A types (Katayama and Karato, 2006). The clear seismic observations of fast S-wave polarizations parallel to plate motion (trench normal) given for the Cascadia (Currie et al., 2004) and Tonga (Fischer et al., 1998) subduction zones, which would be compatible with A or C types. In general, some care has to be taken to separate below slab, slab, and above slab anisotropy components to test mantle wedge anisotropy. The interpretations above follow the logic of Karato et al. (2008), but as mentioned earlier, the role of C-type CPO as indicator of wet olivine is seriously questioned by the experiments of Ohuchi et al. (2012). Most of the reported B-type and C-type CPOs are associated with garnet peridotite bodies and eclogites from UHP metamorphic terranes, for example, the Sulu terrane in China (Xu et al., 2006), Alpe Arami and Cima di Gagnone in the central Alps (Dobrzhinetskaya et al., 1996; Frese et al., 2003; Möckel, 1969; Skemer et al., 2006), Val Malenco peridotite in northern Italy (Jung, 2009), and the Western Gneiss Region of the Norwegian Caledonides (Katayama et al., 2005; Wang et al., 2013).

2.20.3.3 Seismic Anisotropy and Melt

The understanding of the complex interplay between plate separation, mantle convection, adiabatic decompression melting, and associated volcanism at mid-ocean ridges in the upper mantle (e.g., Solomon and Toomey, 1992) and the presence of melt in the deep mantle in the D'' layer (e.g., Williams and

Garnero, 1996) and inner core (Singh et al., 2000) are challenges for seismology and mineral physics. For the upper mantle, two contrasting approaches have been used to study mid-ocean ridges: on one hand marine geophysical (mainly seismic) studies of active ridges and on the other hand geologic field studies of ophiolites, which represent 'fossil' mid-ocean ridges. These contrasting methods have yielded very different views about the dimensions of the mid-ocean ridge or axial magma chambers. The seismic studies have given us three-dimensional information about seismic velocity and attenuation in the axial region. The critical question is, how can this data be interpreted in terms of geologic structure and processes? To do so, we need data on the seismic properties at seismic frequencies of melt containing rocks, such as harzburgites, at the appropriate temperature and pressure conditions. Until recently, laboratory data for filling these conditions were limited for direct laboratory measurements to isotropic aggregates (e.g., Jackson et al., 2002), but deformation of initially isotropic aggregates with a controlled melt fraction in shear (e.g., Holtzman et al., 2003; Zimmerman et al., 1999) allows simultaneous development of the CPO and anisotropic melt distribution. To obtain information concerning anisotropic rocks, one can use various modeling techniques to estimate the seismic properties of idealized rocks (e.g., Mainprice, 1997; Joussetin and Mainprice, 1998; Taylor and Singh, 2002) or experimentally deformed samples in shear (e.g., Holtzman et al., 2003). This approach has been used in the past for isotropic background media with random orientation distributions of liquid-filled inclusions (e.g., Mavko, 1980; Schmeling, 1985a,b; Takei, 2002). However, their direct application to mid-ocean ridge rocks is compromised by two factors. Firstly, field observations on rock samples from ophiolites show that the harzburgites found in the mid-ocean ridges have strong CPOs (e.g., Boudier and Nicolas, 1995), which results in the strong elastic anisotropy of the background medium. For the case of the D'' layer and the inner core, the nature of the background media is not well defined and an isotropic medium has been assumed (Singh et al., 2000; Williams and Garnero, 1996). Secondly, field observations show that melt films tend to be segregated in the foliation or in veins, so that the melt-filled inclusions should be modeled with a shape preferred orientation.

The rock matrix containing melt inclusions is modeled using effective medium theory, to represent the overall elastic behavior of the body. The microstructure of the background medium is represented by the elastic constants of the crystalline rock, including the CPO of the minerals and their volume fractions. Quantitative estimates of how rock properties vary with composition and CPO can be divided into two classes. There are those that take into account only the volume fractions with simple homogenous strain or stress field and upper and lower bounds for anisotropic materials such as Voigt–Reuss bounds, which give unacceptably wide bounds when the elastic contrast between the phases is very strong, such as a solid and a liquid. The other class takes into account some simple aspects of the microstructure, such as inclusion shape and orientation. There are two methods for the implementation of the inclusions in effective medium theory to cover a wide range of concentrations; both methods are based on the analytic solution for the elastic distortion due to the insertion of a single inclusion into an infinite elastic

medium given by Eshelby (1957). The uniform elastic strain tensor inside the inclusion (ε_{ij}) is given by

$$\varepsilon_{ij} = 1/2 (G_{ijkl} + G_{jkil}) C_{klmn} \varepsilon^*_{mn}$$

where G_{ijkl} is the tensor Green's function associated with displacement due to a unit force applied in a given direction, C_{klmn} are the components of the background medium elastic stiffness tensor, and ε^*_{mn} is the eigenstrain or stress-free strain tensor due to the imaginary removal of the inclusion from the constraining matrix. The symmetrical tensor Green's function G_{ijkl} is given by Mura (1987) as

$$G_{ijkl} = \frac{1}{4\pi} \int_0^\pi \sin \theta d\theta \int_0^{2\pi} \left(K_{ij}^{-1}(x) x_k x_l \right) d\phi$$

with $K_{ip}(x) = C_{ijpl} x_j x_l$, the Christoffel stiffness tensor for direction (x) , and $x_1 = \sin \theta \cos \phi/a_1$, $x_2 = \sin \theta \sin \phi/a_2$ and $x_3 = \cos \theta/a_3$.

The angles θ and ϕ are the spherical coordinates that define the vector x with respect to the principal axes of the ellipsoidal inclusion. The semiaxes of the ellipsoid are given by a_1 , a_2 , and a_3 . The integration to obtain the tensor Green's function must be done by numerical methods, as no analytic solutions exist for a general triclinic elastic background medium. Greater numerical efficiency, particularly for inclusions with large axial ratios, is achieved by taking the Fourier transform of G_{ijkl} and using the symmetry of the triaxial ellipsoid to reduce the amount of integration (e.g., Barnett, 1972). The self-consistent (SC) method introduced by Hill (1965) uses the solution for a single inclusion and approximates the interaction of many inclusions by replacing the background medium with effective medium.

In the formulation of SC scheme by Willis (1977), a ratio of the strain inside the inclusion to the strain in the host medium can be identified as A_i :

$$A_i = [I + G(C_i - C^{\text{SCS}})]^{-1}$$

$$\langle \varepsilon^{\text{SCS}} \rangle = \sum_{i=1}^{i=n} V_i A_i \langle \sigma^{\text{SCS}} \rangle = \sum_{i=1}^{i=n} V_i C_i A_i$$

$$C^{\text{SCS}} = \langle \sigma^{\text{SCS}} \rangle \langle \varepsilon^{\text{SCS}} \rangle^{-1}$$

where I is the symmetrical fourth-rank unit tensor, $I_{ijkl} = 1/2 (d_{ik}d_{jl} + d_{il}d_{jk})$, d_{ik} is the Kronecker delta, V_i is the volume fraction, and C_i are the elastic moduli of the i th inclusion. The elastic constants of the SC scheme (C^{SCS}) occur on both sides of the equation because of the strain ratio factor (A), so that solution has to be found by iteration. This method is the most widely used in Earth sciences, being relatively simple to compute and well established (e.g., Kendall and Silver, 1996, 1998). Certain consider that when the SC is used for two phases, for example, a melt added to a solid crystalline background matrix, the melt inclusions are isolated (not connected) below 40% fluid content, and the solid and fluid phases can only be considered to be mutually fully interconnected (biconnected) between 40% and 60%. For our application to magma bodies, one would expect such interconnection at much lower melt fractions. The second method is DEM. This models a two-phase composite by incrementally adding inclusions of melt phase to a crystalline background

phase and then recalculating the new effective background material at each increment. McLaughlin (1977) derived the tensorial equations for DEM as follows:

$$\frac{dC^{\text{DEM}}}{dV} = \frac{1}{(1-V)} (C_i - C^{\text{DEM}}) A_i$$

Here, again the term A_i is the strain concentration factor coming from Eshelby's formulation of the inclusion problem. To evaluate the elastic moduli (CDEM) at a given volume fraction V , one needs to specify the starting value of CDEM and which component is the inclusion. Unlike the SC, the DEM is limited to two components A and B. Either A or B can be considered to be the included phase. The initial value of CDEM is clearly defined at 100% of phase A or B. The incremental approach allows the calculations at any composition irrespective of starting concentrations of original phases. This method is also implemented numerically and addresses the drawback of the SC in that either phase can be fully interconnected at any concentration. Taylor and Singh (2002) attempted to take advantage of both of these methods and minimize their shortcomings by using a combined effective medium method, a combination of the SC and DEM theory. Specifically, they used the formulation originally proposed by Hornby et al. (1994) for shales; an initial melt-crystalline composite is calculated using the SC with melt fraction in the range 40–60% where they claim that each phase (melt and solid) is connected and then uses the DEM method to incrementally calculate the desired final composition that may be at any concentration with a biconnected microstructure.

To illustrate the effect on oriented melt inclusions, I will use the data from the study of a harzburgite sample (90OF22) collected from the Moho transition zone of the Oman ophiolite (Mainprice, 1997). The CPO and petrology of the sample have been described by Boudier and Nicolas (1995), and the CPO of the olivine (AG Type) is given in Figure 26. The mapping area records a zone of intense melt circulation below a fast-spreading paleo-mid-ocean ridge at a level between the asthenospheric mantle and the oceanic crust. I use the DEM effective medium method combined with Gassmann's (1951) poroelastic theory to ensure connectivity of the melt system at low frequency relevant to seismology; see Mainprice (1997) for further details and references. The harzburgite (90OF22) has a composition of 71% olivine and 29% opx. The composition combined with CPO of the constituent minerals and elastic constants extrapolated to simulate conditions of 1200 °C and 200 MPa where the basalt magma would be liquid predicts the following P-wave velocities in principal structural direction: $X = 7.82$, $Y = 7.69$, and $Z = 7.38 \text{ km s}^{-1}$ (X =lineation, Z =normal to foliation, and Y is perpendicular to X and Z). The crystalline rock with no melt has essentially an orthorhombic seismic anisotropy. Firstly, I have added basalt spherical basalt inclusions; the velocities for P- and S-waves decrease and attenuation increases (Figure 30) with increasing melt fraction and the rock becomes less anisotropic, but preserves its orthorhombic symmetry. When 'pancake'-shaped basalt inclusions with $X:Y:Z = 50:50:1$ are added, to simulate the distribution of melt in the foliation plane observed by Boudier and Nicolas (1995), certain aspects of the original orthorhombic symmetry of the rock are preserved, such as

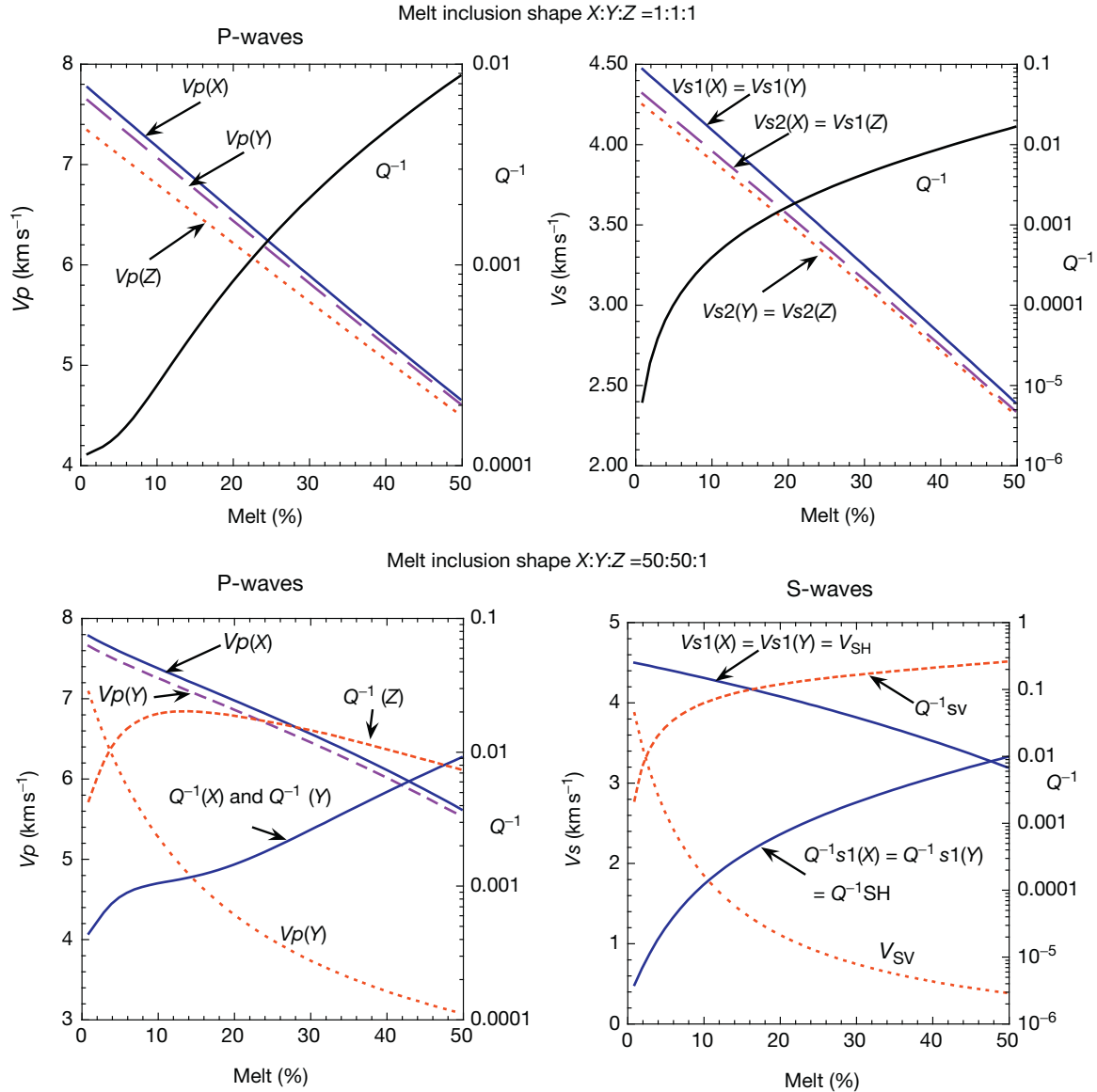


Figure 30 The effect of increasing basalt melt fraction on the seismic velocities and attenuation (Q^{-1}) of a harzburgite. See text for details.

the difference between V_p in the X direction and V_p in the Y direction. However, many velocities and attenuations change illustrating the domination of the transverse isotropic symmetry with Z direction symmetry axis associated with the 'pancake'-shaped basalt inclusions. V_p in the Y direction decreases rapidly with increasing melt fraction, causing the seismic anisotropy of P-wave velocities between Z and X or Y to increase. The contrast in behavior for P-wave attenuation is also very strong with attenuation (Q^{-1}) increasing for Z and decreasing for X and Y directions. For the S-waves, the effects are even more dramatic and more like a transverse isotropic behavior. The S-waves propagating in X direction with a Y polarization, $V_{sX}(Y)$, and Y direction with polarization X , $V_{sY}(X)$ (see Figure 31 for directions), are fast velocities because they are propagating the XY (foliation) plane with polarizations in XY plane; we can call these V_{SH} waves for a horizontal foliation. In contrast, all the other S-waves have either their

propagation or polarization (or both) direction in the Z direction and have the same lower velocity; these we can call V_{SV} . Similarly for the S-wave attenuation, V_{SH} are less attenuated than V_{SV} . From this study, we can see that a few percent of aligned melt inclusions with high axial ratio can change the symmetry and increase the anisotropy of crystalline aggregate (see Figure 31 for summary), completely replacing the anisotropy associated with crystalline background medium in the case of S-waves. Taylor and Singh (2002) came to the same conclusion that S-wave anisotropy is an important diagnostic tool for the study of magma chambers and regions of partial melting.

One of the most ambitious scientific programs in recent years was the mantle electromagnetic and tomography (MELT) experiment that was designed to investigate the forces that drive flow in the mantle beneath a mid-ocean ridge (MELT Seismic Team, 1998). Two end-member models often proposed can be classified into two groups; the flow is a passive

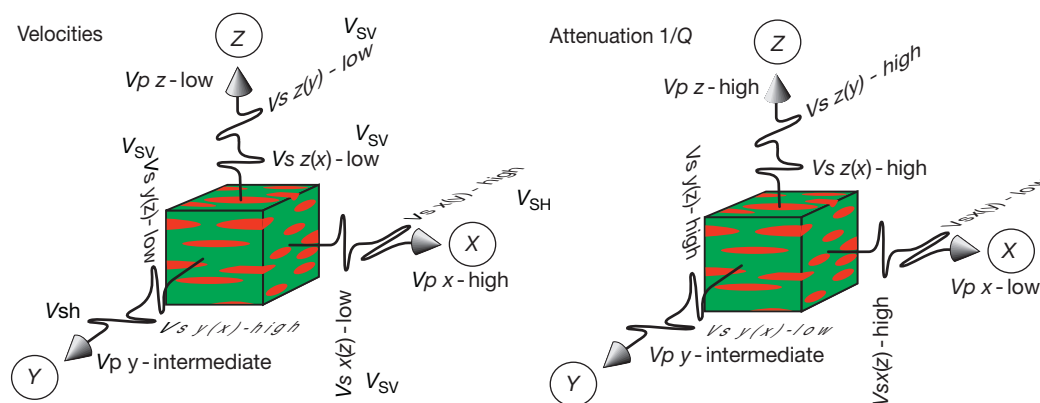


Figure 31 A graphical illustration of the 'pancake'-shaped melt inclusions (red) in the foliation (XY) plane (where X is the lineation) and the relation between velocity and attenuation (Q^{-1}). The melt is distributed in the foliation plane. The velocities have an initial orthorhombic symmetry with $V_p X > Y > Z$. The directions of high velocity are associated with low attenuation. P-waves normal to the foliation have the lowest velocity. S-waves with polarizations in the foliation (XY) plane have the highest velocities (V_{SH}). Diagram inspired a figure in the thesis of Barroul (1993).

response to diverging plate motions, or buoyancy forces supplied a plate-independent component variation of density caused by pressure release partial melting of the ascending peridotite. The primary objective in this study was to constrain the seismic structure and geometry of mantle flow and its relationship to melt generation by using teleseismic body waves and surface waves recorded by the MELT seismic array beneath the superfast-spreading southern East Pacific Rise (EPR). The observed seismic signal was expected to be the product of elastic anisotropy caused by the alignment of olivine crystals due to mantle flow and the presence of aligned melt channels or pockets of unknown structure at depth (e.g., Blackman and Kendall, 1997; Blackman et al., 1996; Kendall et al., 2004; Mainprice, 1997). Observations revealed that on the Pacific Plate (western) side, the EPR had lower seismic velocities (Forsyth et al., 1998; Toomey et al., 1998) and greater shear wave splitting (Wolfe and Solomon, 1998). The shear wave splitting showed that the fast shear polarization was consistently parallel to the spreading direction and at no time parallel to the ridge axis with no null splitting being recorded near the ridge axis. In addition, the delay time between S-wave arrivals on the Pacific Plate was twice that of the Nazca Plate. P delays decreased within 100 km of the ridge axis (Toomey et al., 1998), and Rayleigh surface waves indicated a decrease in azimuthal anisotropy near the ridge axis. Any model of the EPR must take into account that the average spreading rate at 17°S on the ridge is 73 mm year^{-1} and the ridge migrates 32 mm year^{-1} to the west. Anisotropic modeling of the P and S data within 500 km of the ridge axis by Toomey et al. (2002) and Hammond and Toomey (2003) showed that a best fitting finite strain hexagonal symmetry 2-D flow model had an asymmetrical distribution of higher melt fraction and temperature, dipping to the west under the Pacific Plate and lower melt fraction and temperature with an essentially horizontal structure under the Nazca Plate. Hammond and Toomey (2003) introduced low melt fractions ($>2\%$), in relaxed (connected) cusped melt pockets (Hammond and Humphreys, 2000) to match the observed velocities. Blackman and Kendall (2002) used a 3-D texture flow model to predicted pattern of upper mantle flow beneath the EPR oceanic

spreading center with asymmetrical asthenospheric flow pattern. Blackman and Kendall (2002) explored a series of models for the EPR and found that asymmetrical thermal structure proposed by Toomey et al. (2002) produced the model in closest agreement with seismic observations. The 3-D model shows that shear wave splitting will be lowest at about 50 km to the west of the EPR on the Pacific Plate with similar low value at 400 km to the east on the Nazca Plate and not the ridge axis because of the underlying asymmetrical mantle structure. The MELT experiment has showed that melt flow beneath a fast-spreading ridge is more complicated than originally predicted, with a deep asymmetrical structure present to 200 km depth. The influence of the near surface configuration (e.g., ridge migration) was also important in controlling the asthenospheric return flow towards the Pacific superswell in the west (Hammond and Toomey, 2003). The influence of melt geometry appears to be small in the case of the EPR, as the essential anisotropic seismic structure is captured by models that do not have melt geometries with strong shape preferred orientation. The situation may be different for the oceanic crust at fast oceanic spreading centers. The seismic anisotropy in regions of important melt production, such as Iceland (Bjarnason et al., 2002), does not show the influence of melt geometry on anisotropy, but rather the influence of large-scale mantle flow. In other contexts, such as the rifting, for example, the Red Sea (Vauchez et al., 2000) and East African Rift (Kendall et al., 2004), the melt geometry does seem to have an important influence of seismic anisotropy.

2.20.4 Conclusions

In this chapter, I have reviewed some aspects of seismology that have a bearing of the geodynamics of the deep interior of the Earth. In particular, I have emphasized the importance of seismic anisotropy and the variation of anisotropy on a global and regional basis. In the one-dimensional PREM model (Dziewoński and Anderson, 1981), anisotropy was confined to the first 250 km of the upper mantle. Subsequently, other

studies of the mantle found various additional forms of global anisotropy associated with the transition zone, the 670 km boundary layer, and the D'' layer (e.g., Montagner, 1994a,b; Montagner and Kennett, 1996; Montagner, 1998). The most recent global studies using more complete data sets and new methods of analysis emphasize the exceptionally strong nature of the upper mantle anisotropy, the anisotropy of the D'' layer, and no significant deviation from the original isotropic PREM for the rest of the mantle (e.g., Beghein et al., 2006; Panning and Romanowicz, 2006). To explain velocity variations that are observed in the mantle studies using probabilistic tomography places the emphasis on chemical heterogeneity and lateral temperature variations in the mantle (Deschamps and Trampert, 2003; Trampert et al., 2004). Trampert and van der Hilst (2005) argued that spatial variations in bulk major element composition dominate buoyancy in the lowermost mantle, but even at shallower depths, its contribution to buoyancy is comparable to thermal effects. The case of the D'' layer is perhaps even more challenging, as it is clearly a region with not only strong temperature and compositional gradients (e.g., Lay et al., 2004) but also a regionally varying seismic anisotropy (e.g., Maupin et al., 2005; van der Hilst et al., 2007; Wookey et al., 2005a) with an overall global signature (e.g., Beghein et al., 2006; Montagner and Kennett, 1996; Panning and Romanowicz, 2006). The inner core has well-known travel time variations that can be modeled to fit various single or double concentric layered anisotropy scenarios. Some studies (Beghein and Trampert, 2003; Ishii and Dziewoński, 2002) tend to favor a difference in anisotropy between the outermost inner core and innermost inner core; however, they disagree in the magnitude and symmetry of the anisotropy. Calvet et al. (2006) suggested that the data set is too poor to distinguish between several of the current models, whereas new high-quality data (Lythgoe et al., 2014) clearly favor a strongly anisotropic western hemisphere and weakly anisotropic eastern one. Lythgoe et al. (2014) also questioned if the outermost and innermost inner core model is an artifact of not taking into account the hemispherical structure of the inner core. In the mantle and the inner core, there are often differences between studies at the global and regional scales and differences between 1-D and 3-D global models. The seismic sampling over different radial and lateral length scales using surface and body waves of variable frequency has made reference models very important in the reporting and understanding of complex data sets. Kennett (2006) had shown, for example, it is difficult to achieve comparable P- and S-wave definition for the whole mantle. Mineral physics can play important role as a representation based on elastic moduli rather than wave speeds that would provide a better comparator for interpretation in terms of composition, temperature, and anisotropy.

In addressing the basics of elasticity, wave propagation in anisotropic crystals, and the nature of the anisotropy polycrystalline aggregates with CPO, I hope I have provided some of keys necessary for the interpretation of seismic anisotropy. CPO produced by plastic deformation is the link between deformation history and the seismic anisotropy of the Earth's deep interior. We have seen earlier that many regions of the mantle (e.g., lower mantle) do not have a pronounced seismic anisotropy. However, from mineral physics, we have seen that in the upper mantle, olivine has a strong elastic anisotropy; in

the transition zone, wadsleyite is quite anisotropic; in the lower mantle, Mg-perovskite and MgO have increasing anisotropy with depth; in the D'' layer, postperovskite is very anisotropic; and the inner core, hcp iron is moderately anisotropic. In addition, if we add minerals from the hydrated mantle in subduction regions, such as the antigorite, chlorite, talc, and brucite, they can be very anisotropic at low pressure and S-wave anisotropy and can be very high for antigorite and chlorite even at high pressure. Subduction-related nonhydrous minerals, such as Al-CF phase, hollandite I, and stishovite, can have exceptionally high anisotropy in the transition zone and lower mantle. Potentially, the mineralogy suggests that seismic anisotropy could be present if these minerals have a CPO. Aligned melt inclusions and compositional layers can also produce anisotropy. To understand why there are regions in the deep Earth that have no seismic anisotropy is clearly a challenge for mineral physics, seismology, and geodynamics.

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2.21 Properties of Rocks and Minerals: Physical Origins of Anelasticity and Attenuation in Rock

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Nomenclature

A	Measure of anisotropy or interphase variability in elastic moduli or thermal expansivity involved in thermoelastic relaxation strength	D	Diffusivity (of either matter or heat)
a	Spacing between adjacent Peierls valleys	d	Grain size; characteristic separation of vacancy sources
a_d	Period of kink potential measured parallel to dislocation line	D(τ)	Normalized distribution of anelastic relaxation times
B	Dislocation drag coefficient	D_b	Grain-boundary diffusivity
b	Burgers vector	D_B(τ)	Diffusivity for high-temperature background dissipation
C	Rate constant for phase transformation (m s ⁻¹ Pa ⁻¹)	D_k	Kink diffusivity
C_w	Concentration of water (wt ppm)	D_p(ln τ)	Normalized distribution of ln τ to model the dissipation peak associated with elastically accommodated grain-boundary sliding

E	Activation energy for relaxation time	n	Exponent in term βt^n representing transient creep in the Andrade model
E_d	Elastic strain energy per unit length of dislocation or line tension	N_v	Number of dislocation segments of given length L per unit volume
E_P	Activation energy describing position (period) of dissipation peak	p	Internal variable providing link between stress and anelastic strain
E_{up}	Binding energy of dislocation to pinning point	p_0	Stress-dependent equilibrium value of p
f	Frequency; the reciprocal of $du/dx = \tan \phi$ (Figure 4(c))	$p_L(L)$	Distribution of dislocation segment lengths
G	Shear modulus	p_s	Small fluctuation in pressure P
g	Dimensionless multiplier of T_m/T in exponent for thermal activation of relaxation time	Q^{-1}	Inverse quality factor ($=\tan \delta$); a measure of strain energy dissipation
G_{HS}	Mean of the Hashin–Shtrikmann bounds on the shear modulus of a polycrystalline aggregate	Q_D^{-1}	Height of the Debye dissipation peak of the standard anelastic solid
G_m	Free energy of kink migration	r	Exponent describing sensitivity of relaxation time τ_e to water content; radius of minor phase in concentric-sphere model of phase-transforming material
G_R	Relaxed value of shear modulus (anelastic relaxation only)	R	Radius of curvature of dislocation bowed out under applied stress; gas constant; radius of grain-edge tubule
G_{RS}	Reuss average of single-crystal elastic constants for shear	R_e	Outer radius for concentric-sphere model of phase-transforming material
G_U	Unrelaxed shear modulus	s	Laplace transform variable; distance measured along dislocation line; exponent describing grain-size sensitivity of Q^{-1} ; ratio (r/R_e) of radii in concentric-sphere model of phase-transforming material
h	Separation of closely spaced dislocations in subgrain wall	S_m	Entropy of kink migration
$H(x)$	Heaviside step function	t	Time
H_{int}	Kink interaction energy	T	Absolute temperature
h_j	j th coefficient in Fourier series representing grain-boundary topography	T_m	Melting temperature
H_k	Formation energy for a single geometric kink	T_o	Oscillation period ($=2\pi/\omega$)
H_{kp}	Kink-pair formation energy	u	Displacement of dislocation segment, or position of grain boundary, in the y -direction
H_m	Enthalpy of kink migration	$\underline{U}$	Equilibrium distance for grain-boundary sliding
H_{mc}	Activation enthalpy for multicomponent diffusion	$\underline{U}(u)$	Peierls potential
$J(t)$	Creep function	u_0	x -Independent amplitude of u ; position of straight dislocation segment under static stress σ
J^*	Dynamic compliance	u_m	Maximum displacement for newly formed kink pair
J_1	Real part of J^*	V_{SH}	Wave speed for horizontally polarized seismic shear wave
J_2	Negative imaginary part of J^*	V_{SV}	Wave speed for vertically polarized seismic shear wave
J_U	Unrelaxed compliance (ε/σ)	w_k	Width of a single geometric kink
$\bar{K}$	Bulk modulus of composite of coexisting phases	X	Chemical composition
$\bar{k}$	Boltzmann constant	x	Coordinate measuring distance parallel to dislocation line or grain boundary
K_f	Bulk modulus of fluid	x_1	Unstable equilibrium spacing of kinks of opposite sign
K_i	Bulk modulus partially relaxed by phase transformation	y	Coordinate measuring distance perpendicular to dislocation line
K_m	Bulk modulus of melt	Y	Young's modulus
K_R	Bulk modulus fully relaxed by phase transformation	α	Negative of exponent describing frequency dependence of Q^{-1} ; exponent used in specifying the distribution $D(\tau)$ of anelastic relaxation times for the monotonic high-temperature background dissipation
K_s	Bulk modulus of solid matrix	α_b	Aspect ratio of grain-boundary region ($=\delta/d$)
K_U	Unrelaxed bulk modulus		
L	Length of dislocation segment between adjacent pinning points		
$\bar{L}$	Subgrain diameter		
$\bar{L}_c$	Critical dislocation segment length for dislocation multiplication		
M	Ratio (τ_e/τ_d) of characteristic times for elastically and diffusively accommodated grain-boundary sliding		
m_a	Grain-size exponent of anelastic relaxation time		
m_l	Effective mass per unit length of dislocation		
m_v	Grain-size exponent for viscous (Maxwell) relaxation time		
N	Number of terms retained in Fourier series representing grain-boundary topography		

α_e	Aspect ratio (minimum/maximum dimension) of ellipsoidal inclusion	Λ	Dislocation density, that is, dislocation length per unit volume = $N_d L$
α_t	Aspect ratio of grain-edge tubule ($=2R/d$)	Λ_m	Density of mobile dislocations
β	Coefficient of term βt^n representing transient creep in the Andrade model	μ_k	Kink mobility ($=D_k/kT$)
Γ	Gamma function	ν	Poisson's ratio
γ	Multiplicative constant of order unity	ν_{k0}	Attempt frequency of dislocation vibration
γ_s	Multiplicative constant	ρ	Crystal density; dislocation density
Δ	Anelastic relaxation strength	ρ_k^-, ρ_k^+	Densities of kinks of opposite sign (number per unit length of dislocation line)
δ	Phase lag between stress and strain; width of grain-boundary region ($\ll d$)	ρ_{k0}^-, ρ_{k0}^+	Densities of kinks of opposite sign, under conditions of zero stress
$\delta(x)$	Dirac delta function	ρ_k^{eq}	Equilibrium kink density; number of kinks per unit length of dislocation line
Δ_B	Anelastic relaxation strength for high-temperature background dissipation	σ	Stress, usually shear stress; measure of width of normal distribution, $D_p(\ln \tau)$
δG	Anelastic relaxation of the shear modulus	σ_0	Amplitude of sinusoidally time-varying stress
δJ	Anelastic relaxation of the compliance	σ_n	Normal stress
Δ_P	Anelastic relaxation strength for the dissipation peak of elastically accommodated grain-boundary sliding	σ_P	Peierls stress
δP	Width in pressure of binary loop	σ_t	Tectonic shear stress
δT_0	Width of melting interval	σ_{up}	Unpinning shear stress
δT_s	Pressure-induced perturbation to solidus and liquidus temperatures	τ	Relaxation time
Δ_v	Anelastic relaxation strength for the relaxation of the bulk modulus	τ_A	Anelastic relaxation time associated with simple Burgers creep function
$\delta \phi$	Pressure-induced perturbation in melt fraction	τ_d	Duration of transient diffusional creep
$(\delta \rho / \rho)_o$	Fractional density contrast between coexisting polymorphs	τ_{dr}	Timescale for draining of cylindrical laboratory specimen
$(\delta \rho / \rho)_a$	Fractional change in density resulting from small change in proportions of coexisting phases; anelastic volumetric strain	τ_e	Relaxation time for elastically accommodated grain-boundary sliding
$(\delta \rho / \rho)_e$	Fractional change in density caused by pressure p_s	τ_H	Upper cutoff for distribution $D_B(\tau)$ of anelastic relaxation times for high-temperature background
ϵ	Strain	τ_L	Lower cutoff for distribution $D_B(\tau)$ of anelastic relaxation times for high-temperature background
ϵ_0	Amplitude of sinusoidally time-varying strain	τ_M	Maxwell (viscous) relaxation time
ϵ_a	Anelastic strain	τ_P	Relaxation time associated with dissipation peak
ϵ_e	Elastic strain	$\tau_{s,e}$	Relaxation time for melt squirt between ellipsoidal inclusions
ϵ_m	Maximum anelastic strain due to migration of geometric kinks on a dislocation segment	$\tau_{s,t}$	Relaxation time for melt squirt between grain-edge tubules
η	Viscosity or effective viscosity	φ	Grain-boundary slope
η_1	Viscosity of dashpot in parallel with spring in the anelastic element of the Burgers model	ϕ	Melt fraction; the angle between a dislocation segment and its Peierls valley
η_b	Grain-boundary viscosity	ω	Angular frequency
η_f	Fluid viscosity	Ω	Molecular volume of diffusing species
η_m	Melt viscosity	ω_0	(Angular) resonance frequency of dislocation segment
λ	Wavelength of periodic grain-boundary topography or of seismic wave		

2.21.1 Introduction

The Earth and its constituent materials are subjected to naturally applied stresses that vary widely in intensity and time-scale. At sufficiently high temperatures, nonelastic behavior will be encountered – even at the low-stress amplitudes of seismic wave propagation, tidal forcing, and glacial loading (Figure 1). For harmonic loading, nonelastic behavior is manifest in a phase lag between stress and strain, giving rise to strain energy dissipation and associated frequency dependence

(dispersion) of the relevant modulus or wave speed. In the case of glacial loading, the transient creep of mantle material of sufficiently low viscosity allows time-dependent relaxation of the stresses imposed by the growth and decay of ice sheets with consequent time-dependent surface deformations.

Departures from elastic behavior have long been studied in metals. Notable early successes came from the application of resonance (pendulum) methods at fixed frequencies near 1 Hz that revealed low-temperature dissipation peaks attributable to various types of point-defect relaxation (e.g., Nowick and

Berry, 1972; Zener, 1952). Until recently, most of the available information concerning elastic wave speeds in geologic materials and their variations with pressure and temperature came from ultrasonic and optoacoustic techniques (Chapter 2.12) at frequencies at least six orders of magnitude higher than those of teleseismic waves (Figure 1). However, there is growing recognition of the need, first clearly articulated by Goetze (1977), for a thorough understanding of viscoelastic behavior in minerals and rocks at low strains and seismic frequencies. It is the purpose of this chapter to assess the relaxation mechanisms most likely to produce significant departures from elastic behavior under the high-temperature conditions of the Earth's interior. Among these are intragranular mechanisms involving the motion of point defects and dislocations, grain-boundary migration and sliding, stress-induced redistribution of an intergranular fluid phase, and effects associated with phase transformations.

Section 2.21.2 focuses on the theoretical framework for the description of viscoelasticity provided by broad phenomenological considerations and models for the operation of specific microphysical relaxation mechanisms. A thorough review of this subject in a materials science context is provided by Schaller et al. (2001). In Section 2.21.3, an attempt will be made to integrate the results of the still relatively few seismic-frequency laboratory experiments on geologic materials into

the theoretical framework. Section 2.21.4 outlines selected applications of the emerging understanding of viscoelastic relaxation in the interpretation of seismological wave speed and attenuation models.

2.21.2 Theoretical Background

2.21.2.1 Phenomenological Description of Viscoelasticity

For sufficiently small stresses, the stress-strain behavior is expected to be linear and the response is represented in the time domain by the 'creep function' $J(t)$, which is defined as the strain resulting from the application at time $t=0$ of unit step-function stress, that is,

$$\sigma(t) = 0, \quad t < 0 \\ = 1, \quad t \geq 0 \quad [1]$$

(e.g., Nowick and Berry, 1972). For the special case of elastic behavior, the strain appears essentially instantaneously (delayed only by the finiteness of the elastic wave speeds) and, thereafter, remains constant for the duration of stress application. However, at high temperatures and low frequencies, the response $J(t)$ will usually be more complicated than the elastic ideal, involving, in addition to the instantaneous (elastic) component, a time-dependent contribution, which may be a mixture of recoverable (anelastic) and irrecoverable (viscous) strains (Figure 2). The simplest moderately realistic example of such linear viscoelastic rheology, which can be constructed from (elastic) springs and (viscous) dashpots arranged in series and parallel combinations, is the Burgers model (e.g., Cooper, 2003; Findley et al., 1976) with the creep function

$$J(t) = J_U + \delta J[1 - \exp(-t/\tau)] + t/\eta \quad [2]$$

J_U and δJ are the magnitudes of the instantaneous (elastic) and anelastic (time-dependent but recoverable) contributions, whereas τ and η are the time constants for the development of the anelastic response and the steady-state Newtonian viscosity, respectively (Figure 2). The widely used 'standard anelastic solid' (e.g., Nowick and Berry, 1972) is the Burgers model without the series dashpot; its creep function is accordingly given by the first two terms of eqn [2]. More empirically successful in the description of transient creep, but physically less transparent, is the Andrade model (e.g., Poirier, 1985) for which the creep function is

$$J(t) = J_U + \beta t^n + t/\eta, \quad 1/3 < n < 1/2 \quad [3]$$

The middle term with coefficient β and time t raised to the fractional power n represents transient creep. The relative merits of these alternative models as parameterizations of the high-temperature torsional microcreep behavior of our experimental assemblies have recently been evaluated. It has been found that the βt^n term in the Andrade model typically better fits the early part of a torsional microcreep record than does the Burgers model with its unique anelastic relaxation time τ . However, the Burgers model, generalized to include a suitable distribution $D(\tau)$ of anelastic relaxation times,

$$J(t) = J_U \left\{ 1 + \Delta \int_0^\infty D(\tau) [1 - \exp(-t/\tau)] d\tau \right\} + t/\eta \quad [4]$$

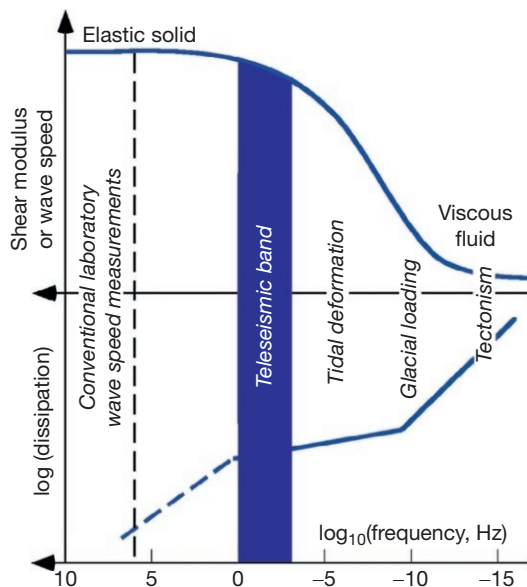


Figure 1 A schematic mechanical relaxation spectrum for the Earth. The mechanical behavior of the Earth's hot interior and its constituent materials changes progressively from that of an elastic solid to that of a viscous fluid with decreasing frequency or increasing timescale. This transition involves the thermally activated mobility of crystal defects including vacancies, dislocations, twin-domain and grain boundaries, and phase boundaries and intergranular melt. The resulting viscoelastic behavior is manifest in the dissipation of strain energy and associated frequency dependence of the shear modulus and wave speed. Adapted from Jackson I, Webb SL, Weston L, and Boness D (2005) Frequency dependence of elastic wave speeds at high-temperature: A direct experimental demonstration. *Physics of the Earth and Planetary Interiors* 148: 85–96.

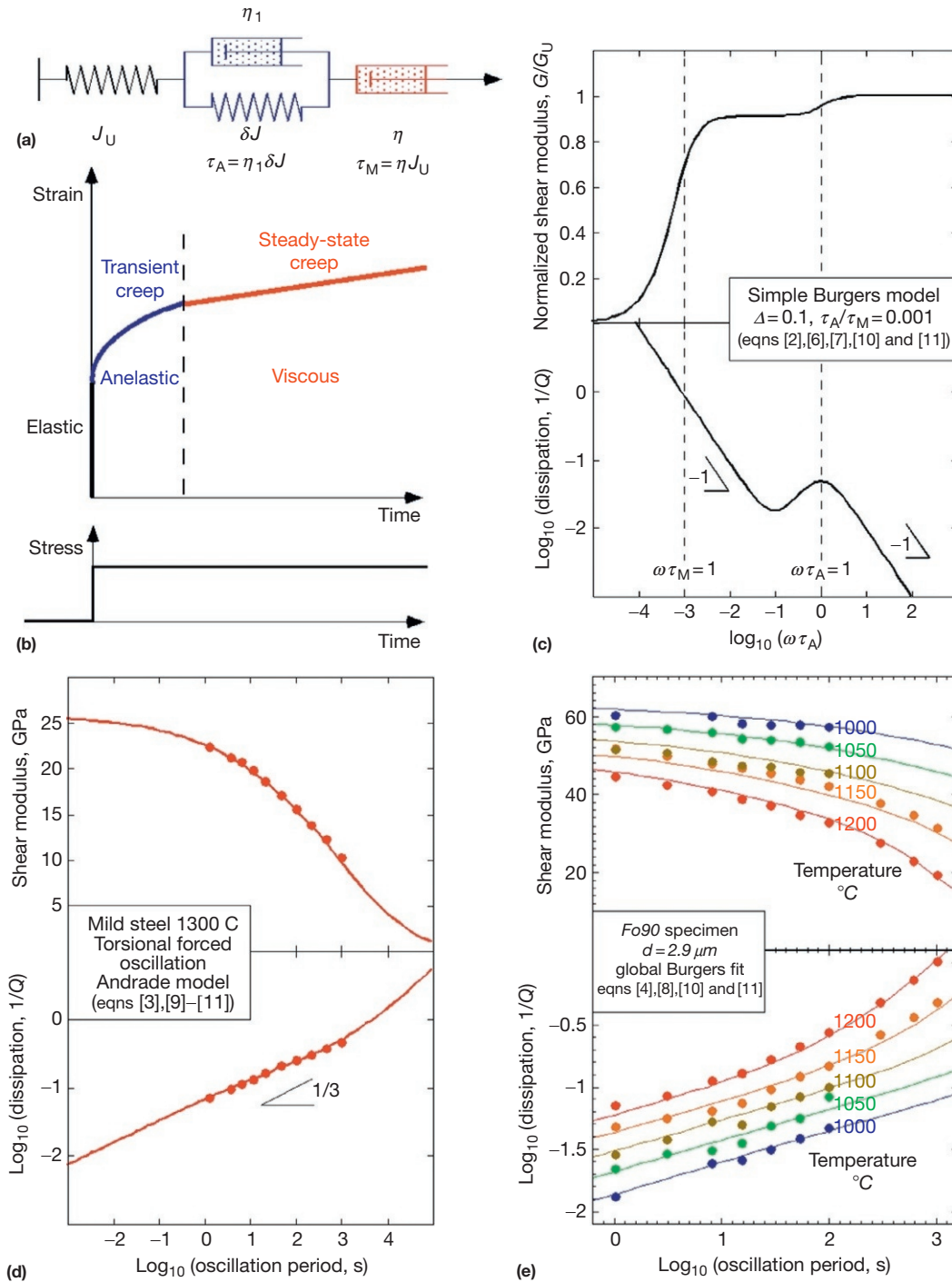


Figure 2 The Burgers and Andrade models for viscoelastic behavior. (a) Construction of the Burgers model from series and parallel combinations of Hookean springs and linear viscous dashpots. (b) The creep function for the Burgers model (eqn [2]). (c) The frequency-dependent shear modulus and dissipation for the Burgers model with $\Delta = 0.1$ and $\tau_M/\tau_A = 10^3$ (eqns [7], [10], and [11]). (d) The variations of shear modulus and dissipation for the Andrade model. The broad absorption band, within which $Q^{-1} \sim T_0^{-n}$ (or ω^{-n}), is the result of the implicit infinitely wide distribution of anelastic relaxation times. This example is the least-squares fit of eqns [3] and [9]–[11] to forced-oscillation data for mild steel tested at 1300 °C and 200 MPa. (e) Another example of a broad absorption band, here for melt-free Fo₉₀ olivine. The data indicated by the plotting symbols are compared with the generalized Burgers model (eqns [4], [8], [10], and [11] with $D(\tau)$ specified by eqn [78]) fitted to such data for a suite of four genuinely melt-free olivine polycrystals. See Faul and Jackson (2005) for details.

provides a versatile alternative to the Andrade model in describing the viscoelastic rheology revealed, for example, by experimental torsional microcreep tests. In eqn [4], Δ is the fractional increase in compliance associated with complete ($t=\infty$) anelastic relaxation, known as the relaxation strength.

The strain $\varepsilon(t) = \varepsilon_0 \exp i(\omega t - \delta)$ resulting from the application of sinusoidally time-varying stress $\sigma(t) = \sigma_0 \exp(i\omega t)$ can be evaluated from the creep function provided that the behavior is linear (i.e., described by a differential equation, which is linear in stress and strain and their respective time derivatives). This is done by superposition of the responses to each of a series of infinitesimal step-function applications of stress, which together represent the history $\sigma(t)$ of stress application (e.g., Nowick and Berry, 1972). Thus, an expression is obtained for the 'dynamic compliance' $J^*(\omega)$ given by

$$J^*(\omega) = \varepsilon(t)/\sigma(t) = i\omega \int_0^\infty J(\xi) \exp(-i\omega\xi) d\xi \quad [5]$$

where $\omega = 2\pi f$ is the angular frequency. This integral is the Laplace transform of $J(t)$ with transform variable $s = i\omega$ or, equivalently, within a multiplicative constant, the Fourier transform of the function, which is $J(\xi)$ for $\xi \geq 0$ and zero elsewhere. Since the Laplace transforms of each of the terms in the Burgers and Andrade creep functions are tabulated in standard compilations (e.g., Abramowitz and Stegun, 1972), analytic expressions for the dynamic compliance are readily derived (e.g., Jackson, 2000).

Thus, the dynamic compliance $J^*(\omega)$ for the simple Burgers model is

$$J^*(\omega) = J_U + \delta J / (1 + i\omega\tau) - i/\eta\omega \quad [6]$$

with real and negative imaginary parts

$$\begin{aligned} J_1(\omega) &= J_U + \delta J / (1 + \omega^2\tau^2) \\ J_2(\omega) &= \omega\tau\delta J / (1 + \omega^2\tau^2) + 1/\eta\omega \end{aligned} \quad [7]$$

For the generalized Burgers model, the equivalent expressions are

$$\begin{aligned} J^*(\omega) &= J_U \left\{ 1 + \Delta \int_0^\infty D(\tau) d\tau / (1 + i\omega\tau) \right\} - i/\eta\omega \\ J_1(\omega) &= J_U \left\{ 1 + \Delta \int_0^\infty D(\tau) d\tau / (1 + \omega^2\tau^2) \right\} \\ J_2(\omega) &= \omega J_U \Delta \int_0^\infty \tau D(\tau) d\tau / (1 + \omega^2\tau^2) + 1/\eta\omega \end{aligned} \quad [8]$$

With the approximations (Nowick and Berry, 1972, pp. 84–87)

$$\begin{aligned} (1 + \omega^2\tau^2)^{-1} &= H[-\ln(\omega\tau)] \\ \omega\tau(1 + \omega^2\tau^2)^{-1} &= (\pi/2)\delta[\ln(\omega\tau)] \end{aligned}$$

where H and δ are the Heaviside step function and Dirac delta function, respectively, eqn [8] can be simplified to obtain

$$\begin{aligned} J_1(\omega) &= J_U \left\{ 1 + \Delta \int_0^{1/\omega} D(\tau) d\tau \right\} \\ J_2(\omega) &= (\pi/2) J_U \Delta D(\tau = 1/\omega) + 1/\eta\omega \end{aligned} \quad [8a]$$

McCarthy et al. (2011) used eqn [8a] to test experimental data $J_1(\omega)$ and $J_2(\omega)$ from forced-oscillation experiments for adherence to the Kronig–Kramers relationship and also to

derive the distribution $D(\tau)$ of anelastic relaxation times without a priori assumption.

For the Andrade model, the expressions corresponding to eqn [8] are

$$\begin{aligned} J^*(\omega) &= J_U + \beta\Gamma(1+n)(i\omega)^{-n} - i/\eta\omega \\ J_1(\omega) &= J_U + \beta\Gamma(1+n)\omega^{-n} \cos(n\pi/2) \\ J_2(\omega) &= \beta\Gamma(1+n)\omega^{-n} \sin(n\pi/2) + 1/\eta\omega \end{aligned} \quad [9]$$

where $\Gamma(1+n)$ is the gamma function (Findley et al., 1976; Gribb and Cooper, 1998a).

From these analytic expressions for $J_1(\omega)$ and $J_2(\omega)$, the shear modulus

$$G(\omega) = [J_1^2(\omega) + J_2^2(\omega)]^{-1/2} \quad [10]$$

and the associated measure of strain energy dissipation

$$Q^{-1}(\omega) = J_2(\omega)/J_1(\omega) \quad [11]$$

are readily evaluated. It follows from eqns [10] and [11] that forced-oscillation measurements of $G(\omega)$ and $Q^{-1}(\omega)$, like the results of microcreep tests, can be represented by a creep-function model in an appropriately internally consistent manner.

In principle, then, knowledge of the creep function $J(t)$ for arbitrary t or of the dynamic compliance $J^*(\omega)$ for arbitrary ω provides equivalent insight into the mechanical behavior of the material. Conversion from one description to the other proceeds through integral transforms such as eqn [5] known as the Kronig–Kramers relations (e.g., Nowick and Berry, 1972, p. 37). These alternative descriptions of the mechanical behavior in the time and frequency domains are naturally associated with microcreep and forced-oscillation experiments, respectively. Practical considerations related to the acquisition and processing of forced-oscillation and microcreep data transform the nature of the relationship between the two methods from strict equivalence to complementarity. Thus, the intensively sampled relatively short-period (<1–1000 s) stress- and strain-versus-time sinusoids of forced-oscillation experiments can be filtered very effectively with Fourier techniques to yield precise determinations of the relative amplitudes and phase of the stress and strain and hence $J^*(\omega)$. For periods longer than 1000 s, however, the acquisition of forced-oscillation records representing a substantial number of oscillation periods becomes prohibitively time-consuming. It is here that the microcreep method has an important advantage. In addition, the capacity to test explicitly the extent of the recovery of the nonelastic strain following removal of the steady stress is a major advantage of the microcreep method.

2.21.2.1.1 Thermodynamic description of anelasticity

Thermodynamic description of anelasticity is based on the notion that stress σ and strain ε are linked not only directly through the unrelaxed modulus $G_U = J_U^{-1}$ but also indirectly through a third, internal, variable p (Nowick and Berry, 1972; Figure 3). If the following conditions are met, the behavior is that of the standard anelastic solid: (1) there exists an equilibrium value $p_0(\sigma)$ of p that is proportional to σ (in the absence of an equilibrium value, the behavior is viscous); (2) $\partial p / \partial t \propto p(t) - p_0$; and (3) the delayed contribution to the strain is proportional to p . There are many different types of internal

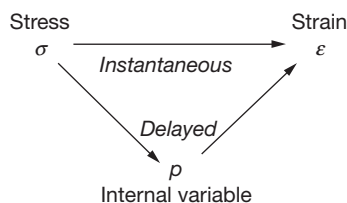


Figure 3 The thermodynamic basis for anelasticity. A third variable p provides an additional indirect and time-dependent link between stress and strain, beyond the connection provided by elasticity. Redrawn after Nowick AS and Berry BS (1972) *Anelastic Relaxation in Crystalline Solids*. New York: Academic Press.

variable potentially associated with anelastic behavior in geologic materials. These include the spatial arrangement of point defects or instantaneous position of a mobile segment of a dislocation line, the position of a mobile twin-domain wall, the pressure in an intergranular fluid phase that is spatially variable at the grain or larger scale, and the proportions and chemical compositions of coexisting mineral phases. Many of these possibilities have been considered elsewhere (e.g., Jackson and Anderson, 1970; Karato and Spetzler, 1990). In this chapter, attention will be focused on those mechanisms most likely to exhibit substantial relaxation strength ($\Delta > 0.001$) at teleseismic and lower frequencies (sub-Hz) under the pressure–temperature conditions of the Earth’s deep interior.

2.21.2.2 Intragranular Processes of Viscoelastic Relaxation

The stress-induced migration or redistribution of defects with thermally activated mobility results in viscoelastic behavior even of single crystals when mechanically tested at sufficiently high temperatures. Such defects include vacancies, interstitials, substitutional impurity atoms, and dislocations.

2.21.2.2.1 Stress-induced rearrangement of point defects

Strain energy dissipation peaks unambiguously associated with the stress-induced migration of point defects have been documented in metals (e.g., Nowick and Berry, 1972). Examples include the stress-induced reorientation of solvent–solute pairs in face-centered cubic (f.c.c.) and other metallic solid solutions (the Zener relaxation), the redistribution of C and other small interstitial atoms in body-centered cubic (b.c.c.) metals such as Fe (the Snoek relaxation), and the stress-induced H diffusion on grain or specimen scale (the Gorsky effect). Such effects might also be expected in mantle minerals – for example, stress-induced repartitioning of Mg and Fe between nonequivalent crystallographic sites. However, relaxation times will generally be very short at mantle temperatures (e.g., < 10 ms at 1000°C for Mg/Fe reordering between adjacent M1 and M2 sites in olivine, Aikawa et al., 1985) and relaxation strengths are typically $< 10^{-3}$ (Karato and Spetzler, 1990).

2.21.2.2.2 Stress-induced motion of dislocations

Dislocation glide has long been recognized as an important mechanism of viscoelastic relaxation in crystalline solids. Theoretical models of the anelasticity associated with the reversible stress-induced glide of dislocation segments located between adjacent pinning points were first developed in the 1950s to

explain low-temperature ($< 0^\circ\text{C}$) internal friction peaks in deformed f.c.c. metals (Granato and Lücke, 1956; Koehler, 1952; Seeger, 1956). Although there was general agreement on the relatively large relaxation strength for this process, the characteristic timescale for the stress-induced motion proved more difficult to estimate reliably because of its dependence on structure and chemical composition of the dislocation core and the interactions among dislocations and between dislocations and impurities.

2.21.2.2.2.1 The vibrating-string model of dislocation damping

An applied shear stress σ exerts a force σb per unit length on a suitably oriented dislocation of Burgers vector b , causing an initially straight dislocation segment to bow out in its glide plane (Figure 4(a)). This tendency is opposed by the line tension or elastic strain energy per unit length $E_d \sim (1/2)Gb^2$, where G is the (unrelaxed) shear modulus. (The consequences of the periodic variation of the elastic strain energy of the dislocation about its average value E_d with position in the crystal lattice will be discussed in the following section.) The balance between the force exerted by the applied stress and the line tension determines the relationship between stress and radius of curvature R of the bowed-out segment as

$$R\sigma = Gb/2 \quad [12]$$

(e.g., Nowick and Berry, 1972). Dislocation segments with length $L < L_c = 2R(\sigma) = Gb/\sigma$ bow out stably under the influence of a static stress σ and will be the primary focus of attention here.

Longer segments ($L > L_c$) participate in dislocation multiplication by the Frank–Read mechanism, thereby increasing the dislocation density and facilitating the transition to power-law dislocation creep. The grain size d imposes an absolute upper limit on the length of dislocation segments. In order to completely exclude the possibility of such dislocation multiplication, and thus guarantee linear behavior, it is accordingly required that

$$\sigma/G < b/d \quad [13]$$

This condition is assessed in Section 2.21.3.1.1, where the applicability of the theory of dislocation relaxation to laboratory experiments and to the Earth’s interior is considered.

The classic vibrating-string dislocation-damping model of Koehler (1952) and Granato and Lücke (1956) has been revisited in simplified form by Nowick and Berry (1972) (see also Fantozzi et al., 1982; Minster and Anderson, 1981; Simpson and Sosin, 1972). A dislocation line with equilibrium orientation parallel to x is pinned by bound impurity atoms or intersections with other dislocations at $x = 0$ and $x = L$ (Figure 4(a)) allowing displacement $u(x, t)$ parallel to y in response to an externally applied oscillating shear stress $\sigma = \sigma_0 \exp(i\omega t)$. The equation of motion expressing the force balance on unit length of dislocation is

$$m_1 \partial^2 u / \partial t^2 + B \partial u / \partial t - E_d \partial^2 u / \partial x^2 = \sigma b = \sigma_0 b \exp(i\omega t) \quad [14]$$

(Granato and Lücke, 1956). In this equation, ρ , $m_1 \sim \rho b^2$, B , and $-1/\partial^2 u / \partial x^2$ are, respectively, the crystal density, the effective mass per unit length of dislocation, the drag coefficient,

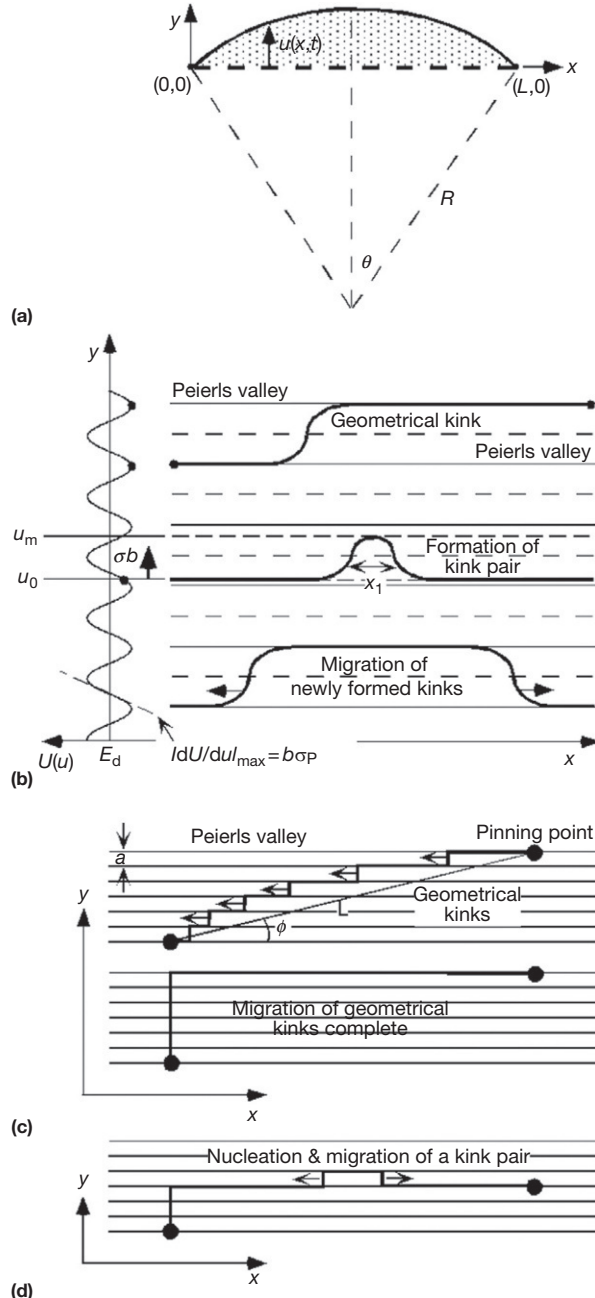


Figure 4 Stress-induced glide of a dislocation segment in response to an externally imposed shear stress σ_{yz} (involving forces parallel to $+y$ ($-y$) acting on the upper (lower) faces of a cube straddling the glide plane in the page). (a) The force exerted on the dislocation by the applied stress and the dislocation line tension are in balance when the dislocation segment has bowed out into an arc with a radius of curvature inversely proportional to the applied stress (eqn [12]). (b) Modulation of the energy of a straight dislocation by the periodic Peierls potential $U(u)$ and its role in the nucleation and migration of kinks (redrawn after Seeger A (1981) The kink picture of dislocation mobility and dislocation-point-defect interactions. *Journal of Physics IV* 42: 201–228). (c) The stress-induced migration from right to left of geometrical kinks contributes a well-defined maximum anelastic strain (eqn [30]). (d) At moderately high temperature, the formation and migration of kink pairs will contribute additional anelastic strain.

and the instantaneous radius of curvature of the dislocation segment.

Neglecting high-frequency perturbations to the shape of the oscillating line segment (treated by Granato and Lücke, 1956), Nowick and Berry (1972, pp. 413–417) derived the approximate solution

$$u(x, t) = u_0(Lx - x^2) \exp(i\omega t) \quad [15]$$

where

$$u_0 = (b\sigma_0/2E_d)/[1 - (\omega/\omega_0)^2 + i\omega\tau] \quad [16]$$

with

$$\omega_0^2 = 12E_d/m_1L^2 \quad [17]$$

and

$$\tau = BL^2/12E_d \quad [18]$$

For a population of N_v dislocation segments per unit volume of common length L and thus a dislocation density (length per unit volume)

$$\Lambda = N_vL \quad [19]$$

the instantaneous value of the anelastic strain, calculated from the area swept out by the population of similarly favorably oriented bowing dislocations, is then

$$\varepsilon_a(t) = (\Lambda b/L) \int_0^L u(x, t) dx = (\Lambda L^2/6) b u_0 \exp(i\omega t) \quad [20]$$

and the resulting anelastic contribution toward the dynamic compliance (eqn [5]) is

$$\begin{aligned} \delta J(\omega) &= \varepsilon_a(t)/\sigma(t) \\ &= (\Lambda b^2 L^2/12E_d)/[1 - (\omega/\omega_0)^2 + i\omega\tau] \end{aligned} \quad [21]$$

For frequencies well below the dislocation resonance frequency ω_0 (estimated from eqn [17] as 20 MHz–2 GHz for $L = 1$ –100 μm in olivine), the behavior is approximately that of the standard anelastic solid (eqn [7] without the $1/\eta\omega'$ term). For $\Lambda \ll 1$, eqns [10] and [11] thus become

$$\begin{aligned} Q^{-1}(\omega) &= \Lambda\omega\tau/(1 + \omega^2\tau^2) \\ \delta G/G &= \Lambda/(1 + \omega^2\tau^2) \end{aligned} \quad [22]$$

with

$$\begin{aligned} \Lambda &= \Lambda G b^2 L^2/12E_d = (1/6)\Lambda L^2 \\ \tau &\sim (1/6)BL^2/Gb^2 \end{aligned} \quad [23]$$

2.21.2.2.2 The role of kinks in dislocation mobility: migration of geometric kinks

However, it is well known that the elastic strain energy of a dislocation is not constant as assumed for the vibrating-string model of dislocation motion but instead varies about the average value E_d with position u within the crystal lattice. The periodic variation normal to the close-packed direction is known as the Peierls potential $U(u)$ (Figure 4(b)). If the Peierls potential is especially large, as is typical of silicate minerals, it will be energetically favorable for a stationary or moving dislocation line to lie mainly within a series of low-energy Peierls valleys – the individual straight segments being offset

a distance a by kinks (Figure 4(b)). The kink picture of dislocation mobility dates from the mid-1950s (Brailsford, 1961; Seeger, 1956; Seeger and Wüthrich, 1976) and has been comprehensively reviewed by Seeger (1981).

We first consider abrupt kinks (of zero width), for which the position $u(x)$ of a dislocation segment of length L is given by

$$u(x) = \int_0^L (\rho_k^- - \rho_k^+) dx \quad [24]$$

where ρ_k^- and ρ_k^+ are the numbers of kinks of opposite sign per unit length of dislocation line. Brailsford (1961) expressed the kink densities as functions of x and t that satisfy continuity equations allowing for the thermal generation and recombination of kinks and for their stress-induced migration and diffusion (with mobility and diffusivity μ_k and D_k , respectively). In this way, he derived a differential equation for the motion of the dislocation segment analogous to eqn [14] with the inertial term neglected

$$\partial u / \partial t - D_k \partial^2 u / \partial x^2 = \sigma b a^2 \mu_k (\rho_k^- + \rho_k^+) \quad [25]$$

A series solution, valid to first order in stress $\sigma_0 \exp(i\omega t)$, was obtained by fixing ρ_{k0}^- and ρ_{k0}^+ at their zero-stress levels, ρ_{k0}^- and ρ_{k0}^+ , respectively. The dominant leading term is of the form

$$u(x, t) - u_0 = u_1 \sin(\pi x / L) \exp(i\omega t) / (1 + i\omega \tau_L) \quad [26]$$

Substitution into eqn [25] and integration with respect to x allows evaluation of the anelastic relaxation time and relaxation strength associated with the motion of preexisting (geometric) kinks as

$$\tau = (L/\pi)^2 / D_k \sim (L/\pi a_d)^2 \times [v_{k0} \exp(S_m/k)]^{-1} \exp(H_m/kT) \quad [27]$$

and

$$\begin{aligned} \Delta &= (8/\pi^4) AL^2 (ab^2 G/kT) \times a(\rho_{k0}^- + \rho_{k0}^+) \\ &\sim (4/5\pi^4) AL^2 (ab^2 G/kT) \end{aligned} \quad [28]$$

(Brailsford, 1961; see also Fantozzi et al., 1982; Seeger, 1981; Seeger and Wüthrich, 1976). The kink diffusivity D_k in eqn [27] is given approximately by

$$D_k = a_d^2 v_{k0} \exp(-G_m/kT) \quad [29]$$

where $G_m = H_m - TS_m$ is the free energy of kink migration, v_{k0} is the attempt frequency of dislocation vibration, and $a_d \sim b$ is the period of the kink potential. Equation [28] gives the relaxation strength for a population of dislocations with dislocation density Δ and uniform segment length L with an average value of $a(\rho_{k0}^- + \rho_{k0}^+) \sim \tan \phi$ of 1/10 (ϕ is the inclination of the dislocation line from the Peierls valley; Brailsford, 1961).

Importantly, this analysis of dislocation relaxation based on migration of geometric kinks yields the same key scalings, whereby $\Delta \propto AL^2$ and $\tau \propto L^2$, as the vibrating-string model (Fantozzi et al., 1982; eqn [23]). The mild temperature dependence of Δ arises from the ratio of kink mobility to diffusivity.

From Figure 4(c), it is clear that the maximum area swept out by migration of geometric kinks on a dislocation segment of length L is given by $L^2 \sin \phi \cos \phi / 2$. The maximum anelastic strain resulting from the migration of geometric kinks

$$\epsilon_m = bAL \sin \phi \cos \phi / 2 \quad [30]$$

(e.g., Karato, 1998) will be compared with the strains of laboratory experiments and seismic wave propagation in a later section.

2.2.2.2.3 The role of kinks in dislocation mobility: formation and migration of kink pairs

The more elaborate analysis of Seeger (1981) includes a quantitative description of the finite width of kinks and the formation and migration of new kink pairs in the stressed crystal. The starting point is the time-independent force balance per unit length of dislocation (cf. eqn [14]) with the additional restoring force tending to constrain dislocation segments to lie in the Peierls valleys

$$E_d d^2 u / dx^2 - dU/du + \sigma b = 0 \quad [31]$$

Under a static stress σ , a straight dislocation in equilibrium will thus occupy a position u_0 such that

$$(dU/du)|_{u=u_0} = b\sigma \quad [32]$$

and the maximum value of $|dU/du|$ is thus associated with the Peierls stress σ_P (Figure 4(b)).

A more general solution involving kinks is sought by rewriting $d^2 u / dx^2$ in eqn [31] as $-(1/f^3) df/du$, where $f = dx/du$. Integration then yields

$$\begin{aligned} 1/f^2 &= (2/E_d) \int_{u_0}^{u_m} [dU/du - \sigma b] du \\ &= (2/E_d) [U(u_m) - U(u_0) - \sigma b(u_m - u_0)] \end{aligned} \quad [33]$$

The requirement that $1/f(u_m) = 0$ means that u_m must satisfy

$$U(u_m) - U(u_0) - \sigma b(u_m - u_0) = 0 \quad [34]$$

with the understanding that for $\sigma = 0$, $u_0 = 0$ and $u_m = a$.

The shape of either a positive or negative geometric kink ($\sigma = 0$) or a kink pair ($\sigma \neq 0$) is then obtained by further integration as

$$\begin{aligned} x - x_0 &= \int_{u_0}^{u_m} f(u) du = \pm (2/E_d)^{-1/2} \\ &\times \int_{u_0}^{u_m} [U(u) - U(u_0) - \sigma b(u - u_0)]^{-1/2} du \end{aligned} \quad [35]$$

This powerful general result (Seeger, 1981, eqn [5]) provides the basis for a detailed description of the role of kinks in anelastic relaxation. Both preexisting (geometric) kinks and newly formed kink pairs may contribute. The following is a brief outline of the way in which estimates of relaxation strength Δ and relaxation time τ have been derived through considerations based on eqn [35]. In order to illustrate key aspects of the theory, some results are evaluated for a specific (sinusoidal) functional form for the Peierls potential

$$U(u) = U(0) + (a/2\pi) b \sigma_P [1 - \cos(2\pi u/a)] \quad [36]$$

along with the approximations $a \sim b$ and $E_d \sim (1/2)Gb^2$.

The energy of formation H_k and width w_k of a single geometric kink are

$$\begin{aligned} H_k &= \int_{-\infty}^{\infty} \{E_d [ds/dx - 1] + [U(u) - U(0)]\} dx \\ &= (2E_d)^{1/2} \int_0^u [U(u) - U(0)]^{1/2} du \end{aligned} \quad [37]$$

with $ds = (dx^2 + du^2)^{1/2}$ and

$$w_k = a|dx/du|_{u=a/2} = 2a^2 E_d / \pi H_k \quad [38]$$

For the sinusoidal Peierls potential (eqn [36]), these expressions can be evaluated as

$$H_k = (2a/\pi)(2ab\sigma_P E_d / \pi)^{1/2} \sim (2/\pi^{3/2})Gb^3(\sigma_P/G)^{1/2} \quad [39]$$

and

$$w_k = (\pi^{1/2}/2)b(\sigma_P/G)^{-1/2} \quad [40]$$

The functional forms of eqns [39] and [40] illustrate the close relationship between the Peierls stress and the geometry and energetics of kink formation. The higher the Peierls stress, the narrower are the kinks and the greater is their formation energy.

Allowance for the work done against the external stress in forming a kink pair yields

$$H_{kp} = 2(2E_d)^{1/2} \int_{u_0}^{u_m} [U(u) - U(u_0) - \sigma b(u - u_0)]^{1/2} du < 2H_k \quad [41]$$

An estimate of the kink-pair formation energy that is more accurate for low-stress conditions ($\sigma/\sigma_P \ll 1$) corresponds to the unstable equilibrium spacing x_1 of kinks of opposite sign at which their interaction energy H_{int} is maximized:

$$H_{kp} = 2H_k - H_{int}(x_1) \quad [42]$$

Under these conditions, there is a balance between the forces associated with the applied stress and the forces associated with the long-range elastic interaction seeking, respectively, to increase and decrease the kink separation (Figure 4(b)).

Analysis of the statistical mechanics of the dislocated crystal (with and without kinks) leads to estimates of the entropy of kink formation, the kink-pair formation rate, and hence the equilibrium density of kinks of given sign per unit length of dislocation line, given by

$$\rho_k^{eq} = (1/w_k)(2\pi H_k/kT)^{1/2} \exp(-H_k/kT) \quad [43]$$

(for the sinusoidal potential). The velocity of a dislocation moving perpendicular to its Peierls valley by the formation and separation of kink pairs is then calculated. Finally, expressions are obtained for the relaxation strength

$$\Delta = AL^2 b^2 G_u / 12E_d \sim (1/6)AL^2 \quad [44]$$

and the relaxation time

$$\tau = [kT/(\rho_k^{eq})^2 D_k] (L/2a^2 E_d)(1 + \rho_k^{eq} L) \quad [45]$$

(eqns [45] and [50] of Seeger, 1981). The latter applies to conditions of stress sufficiently low for the temperature-dependent equilibrium kink density to be maintained and for all but very low temperatures (<10 K). It follows from eqns [29], [43], and [45] that different effective activation energies of approximately $2H_k + H_m$ and $H_k + H_m$ are expected for the low- and high-temperature regimes, respectively, defined by $\rho_k^{eq} L \ll 1$ and $\rho_k^{eq} L \gg 1$, respectively. The lower activation energy $H_k + H_m$ for the high-temperature

regime reflects the greater probability of kink annihilation at high kink densities.

The relaxation strength (eqn [44]) is identical to that for the vibrating-string model (eqn [23]) as expected from geometric considerations. At the high kink densities of the high-temperature regime ($\rho_k^{eq} L \gg 1$), the relaxation time given by eqn [45] is equivalent to eqn [23] for the vibrating-string model with the drag coefficient $B = 6kT/\rho_k^{eq} D_k a^2$, reasonably, inversely proportional to the product of the kink density and kink mobility (D_k/kT).

2.21.2.2.2.4 Relaxation strength for dislocation damping

The foregoing analysis (eqns [23] and [44]) yields a substantial relaxation strength $\Delta \sim 0.1$ – 1 for the stress-induced migration of favorably oriented intragranular dislocation segments with the dislocation density $\Lambda \sim L^{-2}$ of a three-dimensional (3D) (Frank) network. A relaxation strength of order unity for olivine at upper-mantle temperatures is similarly expected from eqn [28] for relaxation due to the motion of geometric kinks if the dislocation density approaches that of the Frank network. Somewhat lower values of $\Delta \sim 0.01$ – 0.1 are inferred once allowance is made for more typical geometries. However, for dislocations closely spaced (separation h) in the walls of subgrains of dimension L , the predicted relaxation strength is enhanced relative to that for a Frank network by the factor L/h , which can be substantially >10 (Friedel et al., 1955; Nowick and Berry, 1972).

2.21.2.2.2.5 Absorption band behavior: distribution of relaxation times

The foregoing theory is readily generalized to accommodate a wide distribution of dislocation segment lengths (e.g., Schoeck, 1963). If $p_L(L)dL$ is the number of dislocation segments per unit volume of length between L and $L+dL$, then the total dislocation length per unit volume is

$$\Lambda = \int_0^\infty p_L(L)LdL \quad [46]$$

The internal friction and frequency-dependent modulus are, respectively,

$$Q^{-1}(\omega) = \Delta \int_0^\infty p_L(L)L^3 \omega \tau(L)dL / [1 + \omega^2 \tau^2(L)] \quad [47]$$

and

$$G(\omega)/G_u = 1 - \Delta \int_0^\infty p_L(L)L^3 dL / [1 + \omega^2 \tau^2(L)] \quad [48]$$

where Δ is now the anelastic relaxation strength for the entire distribution of dislocation segment lengths.

For geologic materials tested in the laboratory, the dissipation commonly displays a monotonic variation of Q^{-1} with frequency and temperature represented by

$$Q^{-1} \sim [\omega \exp(E/RT)]^{-\alpha} \quad [49]$$

with $\alpha \sim 0.3 \pm 0.1$ (Berckheimer et al., 1982; Gribb and Cooper, 1998a; Jackson and Faul, 2010; Jackson et al., 2002). Geophysical observations of the attenuation of seismic body and surface waves and free oscillations, and of strain energy dissipation at the longer periods of Earth tides

and the Chandler wobble, are broadly consistent with this view of the frequency dependence of Q^{-1} (e.g., [Minster and Anderson, 1981](#); [Shito et al., 2004](#); [Chapter 1.25](#)). It should be noted, however, that systematically lower values of α for frequencies below 0.005 Hz, becoming negative below 0.001 Hz, have recently been suggested from an analysis of surface wave and normal mode data intended to eliminate the trade-off between the frequency and depth dependencies of dissipation ([Lekić et al., 2009](#)). If eqn [47] with $\tau(L) \sim L^2$ (e.g., eqns [23], [27], and [45]) is to yield $Q^{-1} \sim \omega^{-\alpha}$, it is required that the distribution of dislocation segment lengths adopt the form

$$p_L(L) \sim L^{2\alpha-4} \quad [50]$$

strongly skewed toward short dislocation lengths ([Karato, 1998](#); [Minster and Anderson, 1981](#)). Alternatively, or additionally, a distribution of activation energies for dislocation migration might contribute to the breadth of an anelastic absorption band ([Minster and Anderson, 1981](#)).

2.21.2.2.2.6 Dislocation relaxation: transition from anelastic to viscous behavior

The foregoing analysis is based on the assumption that dislocation segments are firmly pinned by bound impurities and/or interactions with other dislocations. Under these circumstances, the restoring force provided by line tension or recovery of kink-pair formation energy ensures that the nonelastic strain is recoverable upon removal of the applied stress, meaning that the behavior is anelastic. However, at sufficiently high temperatures and/or stress amplitudes, dislocation segments may break free from their pinning points, thereby allowing larger, irrecoverable (viscous) strains. By balancing the work done in moving the dislocation away from the pinning point with the binding energy E_{up} of the dislocation to the pinning point, the critical stress σ_{up} for unpinning (at 0 K) can be estimated as

$$\sigma_{up} = E_{up}/abL \quad [51]$$

For finite temperature T , thermal activation will allow unpinning at somewhat lower stresses with a probability proportional to $\exp[-(E_{up} - \sigma abL)/kT]$ ([Nowick and Berry, 1972](#), pp. 364–365).

2.21.2.2.2.7 Role of water in nominally anhydrous minerals

The presence of intragranular water (or more accurately hydrogen-related defects) is known to affect both large-strain rheology and electrical conductivity of nominally anhydrous silicate minerals like olivine and wadsleyite. Arguing mainly by analogy with such observations, [Karato and Jung \(1998\)](#) (see also [Chapter 9.05](#)) suggested that water with concentration C_W within mineral grains and/or grain boundaries might similarly enhance seismic wave attenuation and dispersion through its influence on the concentrations and mobilities of key defects. For parameterization, they suggested a variant of eqn [49]:

$$Q^{-1} \sim [(A + BC_W)/\omega \exp(gT_m/T)]^\alpha \quad [52]$$

in which T_m is the relevant melting temperature and g is a dimensionless constant.

2.21.2.3 Intergranular Relaxation Processes

2.21.2.3.1 Effects of elastic and thermoelastic heterogeneity in polycrystals and composites

The role of the heterogeneous microscopic stress field that arises in stressed polycrystals as the inevitable consequence of the elastic anisotropy of the component crystallites has been somewhat neglected in discussions of the nature of the high-temperature internal friction background. During testing under conditions of high temperature and low frequency, these intergranular fluctuations in stress may be subject to relaxation by the reversible migration of grain boundaries ([Leak, 1961](#)). Such grain-boundary migration is driven by the minimization of the elastic strain energy of the stressed polycrystal ([Kamb, 1959](#)). The anelastic relaxation involves enlargement of those grains oriented for high compliance under the prevailing stress relative to neighboring grains oriented for lower compliance ([Nowick and Berry, 1972](#), p. 453; [Figure 5](#)).

A useful indication of the magnitude of the modulus relaxation ([Kumazawa, 1969](#)) derives from consideration of the physical basis for the Voigt and Reuss bounds on the effective elastic moduli of a polycrystal. In such discussions, the Reuss (lower) bound on the effective moduli assumes special significance because it corresponds to a state of uniform stress throughout the polycrystal. It is just this condition that is approached through relaxation of the initially inhomogeneous internal stress field. Kumazawa therefore concluded that the difference between the Voigt–Reuss–Hill (or the average G_{HS} of the more closely spaced Hashin–Shtrikmann bounds) and Reuss averages (G_{RS}) of the single-crystal elastic constants is a measure of the inherent nonelastic behavior of the polycrystal. Thus, the fractional relaxation of the shear modulus is given by

$$\delta G/G = (G_{HS} - G_{RS})/G_{HS} \quad [53]$$

Shear moduli intermediate between G_{HS} and G_{RS} can accordingly be achieved through the relaxation toward uniformity of the inhomogeneous internal stress field arising from the elastic anisotropy of the individual crystallites.

Elastic heterogeneity in polycrystals and multiphase composites leads also to bulk dissipation Q_K^{-1} arising from the coupling between macroscopic volumetric and internal shear strains ([Budiansky and O'Connell, 1980](#)). Their estimates of Q_K^{-1}/Q_G^{-1} for representative upper-mantle materials will be considered in [Section 2.21.4](#). The magnitude of Q_K^{-1} and the

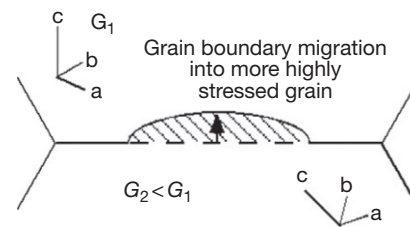


Figure 5 Reversible stress-induced grain-boundary migration as an anelastic relaxation mechanism. The driving force for the (normal) migration of the boundary is the reduction of elastic strain energy. Redrawn after Jackson I, Fitz Gerald JD, and Kokkonen H (2000) High-temperature viscoelastic relaxation in iron and its implications for the shear modulus and attenuation of the Earth's inner core. *Journal of Geophysical Research* 105: 23605–23634.

extent of the associated relaxation of the bulk modulus depend on the spacing between the *HS*-average and Reuss bounds on the effective bulk modulus (cf. eqn [53]). These are typically much more closely spaced than for the shear modulus resulting in more modest anelastic relaxation of the bulk modulus (Section 2.21.4).

Anisotropy and interphase variability (collectively, heterogeneity) of elastic constants and thermal expansivity within polycrystals and composite materials result in spatial heterogeneity of the temperature changes caused by adiabatic compression that may be relaxed toward isothermal conditions by intergranular or interphase heat flow (Budiansky et al., 1983; Zener, 1952). A formal phenomenological theory (Zener, 1952, pp. 84–89) for such thermoelastic behavior, valid at frequencies sufficiently high for the diffusion of heat to be confined to the immediate neighborhood of the grain or interphase boundaries, yields

$$Q^{-1} \sim A(D/\omega)^{1/2}/d \quad [54]$$

(cf. eqn [49]), where D is the thermal diffusivity and d is the grain size. The dissipation scales with the measure A of the heterogeneity of the relevant physical property. The relevance of thermoelastic damping to bulk dissipation Q_K^{-1} in the Earth's mantle will be considered briefly in Section 2.21.4.

2.21.2.3.2 Grain-boundary sliding

2.21.2.3.2.1 Overview

Grain-boundary sliding has been widely invoked as a plausible mechanism for the ubiquitous transition from elastic through anelastic to viscous behavior in fine-grained polycrystalline materials. Central to the theory of grain-boundary sliding is the notion of a grain-boundary region, of finite width δ , distinguished from the crystalline lattices of the neighboring grains by a higher degree of positional disorder and, consequently, higher diffusivities D_b for the various atomic and molecular species and lower effective viscosity η_b . At sufficiently low temperature and/or high frequency of stress application, grain-boundary sliding will be inhibited, and an unrelaxed shear modulus G_U representative of the strictly elastic behavior of the polycrystal is expected (Figure 6(a)). With increase of temperature and/or timescale of the mechanical test beyond an appropriate threshold, it is envisaged that relaxation (to zero) of the distribution of grain-boundary shear stress allows a finite amount of sliding along suitably oriented boundaries accommodated by elastic distortion of the neighboring grains (Ashby, 1972). The modified distribution of normal stress associated with the accommodating elastic distortion provides the restoring force required for macroscopically anelastic (i.e., recoverable) behavior (Figure 6(b)). At still longer timescales and higher temperatures, it is envisaged that viscous deformation occurs with grain-boundary sliding accommodated by diffusional transport of matter away from boundary regions of high chemical potential (normal stress) to other parts of the grain-boundary at lower chemical potential (Raj and Ashby, 1971). The transition from the anelastic behavior associated with elastically accommodated grain-boundary sliding to steady-state viscous behavior requires an adjustment of the distribution of normal stress that is facilitated by grain-boundary diffusion (Figure 6(c)).

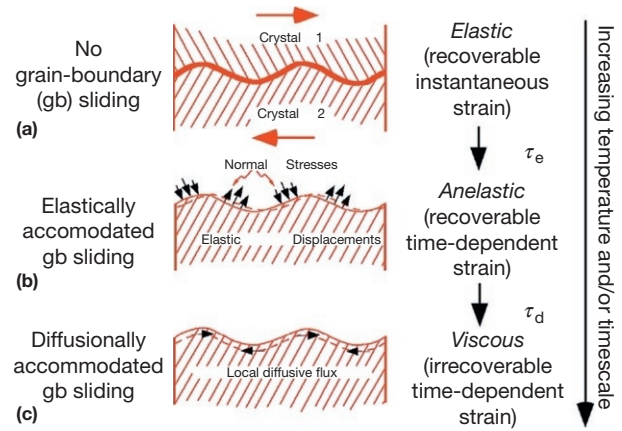


Figure 6 Grain-boundary sliding as a viscoelastic relaxation mechanism. The low effective viscosity of the grain-boundary region facilitates local shear stress relaxation and sliding providing for a seamless transition with increasing temperature and/or timescale from elastic through anelastic to viscous behavior as described in the text. Adapted from Ashby MF (1972) Boundary defects and atomistic aspects of boundary sliding and diffusional creep. *Surface Science* 31: 498–542.

2.21.2.3.2.2 Elastically accommodated grain-boundary sliding

The elastic regime prevailing following the completion of elastically accommodated sliding was analyzed in the classic work of Raj and Ashby (1971). The component of the normal stress parallel to the mean direction x of the grain boundary and integrated over the wavelength λ of the periodic boundary balances the externally applied shear stress σ . The elastic strains caused by the newly created distribution of normal stress are those required to restore grain shape compatibility across the slipped boundary and were calculated in the approximation of infinitesimal boundary slope. With the boundary topography $u(x)$ for a 2D array of hexagonal grains (of unrelaxed shear modulus G_U and Poisson's ratio ν) represented by a Fourier series

$$u(x) = \sum_{j=1}^{\infty} h_j \cos(2\pi jx/\lambda) \quad [55]$$

the following expressions were obtained for the normal stress σ_n and the equilibrium distance U of reversible sliding:

$$\sigma_n(x) = -\sigma\lambda \sum_{j=1}^{\infty} j^2 h_j \sin(2\pi jx/\lambda) / \left[\pi \sum_{j=1}^{\infty} j^3 h_j^2 \right] \quad [56]$$

$$U = (1-\nu)\lambda^3 \sigma / \left[2\pi^3 G_U \sum_{j=1}^{\infty} j^3 h_j^2 \right] \quad [57]$$

Numerical results, apparently based on truncation of the infinite series after $N=100$ terms, yielded a finite sliding distance and a corresponding large anelastic relaxation strength

$$\Delta = 0.57(1-\nu) \quad [58]$$

independent of grain size. For example, for $\nu=0.26$, appropriate for olivine at 1000–1300 °C (Anderson and Isaak, 1995), $\Delta \sim 0.42$. The relaxed shear modulus G_R and the height Q_D^{-1} of

the Debye dissipation peak (as appropriate for the standard anelastic solid) are given by the following expressions:

$$G_R/G_U = 1/(1 + \Delta), \quad Q_D^{-1} = (\Delta/2)/(1 + \Delta)^{1/2} \quad [59]$$

However, because $h_j \sim j^{-2}$ (Raj, 1975), the infinite sum $\sum j^3 h_j^2$ in the denominators of eqns [56] and [57] fails to converge – suggesting that sufficiently sharp grain-edge intersections might inhibit elastically accommodated sliding (Faul et al., 2004; Jackson et al., 2006). The higher values of $\Delta \sim 0.8$ obtained in the modeling of sliding between spherical grains (Kê, 1947; Zener, 1941) and the lower values (0.23 for $\nu = 0.26$) reported from a finite-element study with a fine mesh (Ghahremani, 1980) are consistent with this suggestion.

The relaxation time for elastically accommodated grain-boundary sliding is given by

$$\tau_e = \gamma \eta_b d / G_U \delta \quad [60]$$

where γ , of order one, is either a constant or a function of Poisson's ratio ν for the unrelaxed material (Ghahremani, 1980; Kê, 1947; Mosher and Raj, 1974; Nowick and Berry, 1972; O'Connell and Budiansky, 1977).

2.21.2.3.2.3 Diffusionally accommodated grain-boundary sliding

The possibilities of elastic and steady-state diffusional accommodation of grain-boundary sliding were examined separately by Raj and Ashby (1971). Grain-boundary sliding with 'sequential' occurrence of elastic and diffusional accommodation was explored by Raj (1975) in his analysis of transient diffusional creep. The transient required to adjust the normal stress distribution from that prevailing on completion of elastically accommodated sliding (eqn [56]) to that required for steady-state diffusional creep is of approximate duration

$$\tau_d = (1 - \nu) k T d^3 / [40 \pi^3 G_U \delta D_b \Omega] \quad [61]$$

where Ω is the molecular volume of the diffusing species and D_b is the grain-boundary diffusivity. The transient-creep rate calculated by Raj is enhanced relative to the corresponding steady-state diffusional creep rate by a numerical factor that varies approximately as $(t/\tau_d)^{-1/2}$, which integrates to a creep function of the Andrade form (eqn [3]) – as recognized and emphasized by Gribb and Cooper (1998a) (see also Cooper, 2003). This creep function implicitly involves a monotonic and infinitely wide distribution of anelastic relaxation times (Jackson, 2000) and therefore does not result in a dissipation peak. The diffusional creep transient should instead be responsible for a wide anelastic absorption band, within which

$$Q^{-1} \sim T_0^{1/2} d^{-s} \quad [62]$$

with period $T_0 = 2\pi/\omega$ and $1 < s < 3/2$ (Faul et al., 2004; Gribb and Cooper, 1998a).

Through the use of the well-known connection between grain-boundary diffusivity and viscosity, it can be shown that $M = \tau_e/\tau_d \ll 1$. Thus, it is predicted that the dissipation peak associated with the transition between elastic and anelastic behavior and the onset of viscous behavior should be widely separated in oscillation period – temperature space (Jackson et al., 2002).

2.21.2.3.2.4 The Raj–Ashby model revisited

However, intensive laboratory studies of fine-grained geologic and ceramic materials (Section 2.21.3.3.2) reveal a consistent pattern of high-temperature viscoelastic behavior that differs from the classic Raj–Ashby theory in two main respects: (i) dissipation peaks of amplitude significantly $> 10^{-2}$ are not observed for melt-free materials and (ii) the dominant dissipation background is generally more mildly frequency- and grain size-sensitive than expected of transient diffusional creep (eqn [62]). Accordingly, the classical Raj–Ashby model of grain-boundary sliding has recently been subjected to further scrutiny with a combination of analytic and numerical (finite-element) methods (Lee and Morris, 2010; Lee et al., 2011; Morris and Jackson, 2009). This work, recently reviewed by Jackson et al. (2014), provides an instructive model for the complete mechanical relaxation spectrum resulting from grain-boundary sliding in fine-grained materials. A dissipation peak located at $\omega \sim 1/\tau_e$ and the diffusional accommodation regime with $Q^{-1} \sim \omega^{-1}$ for $\omega < 1/\tau_d$ are separated by a diffusional assisted sliding regime within which Q^{-1} varies mildly with frequency (Figure 7(a)), with associated relaxation of the shear modulus (Figure 7(b)). Within this regime, diffusion occurs on progressively greater spatial scales (ultimately comparable with the grain size d) with decreasing frequency toward $1/\tau_d$.

For finite slopes of the periodic piecewise-linear boundary between elastic grains, like the 30° sawtooth boundary for which results are shown in Figure 7, elastically accommodated sliding results in a dissipation peak of amplitude ~ 0.05 – an order of magnitude lower than that for the infinitesimal-slope solution (Morris and Jackson, 2009; Raj and Ashby, 1971). The dissipation peak is broadened and further diminished in amplitude by any spatial heterogeneity in grain size and/or grain-boundary viscosity. For example, fourfold variation in grain size and tenfold variation of boundary viscosity, in combination, result in a height of ~ 0.02 for the broadened peak associated with elastically accommodated sliding (Lee and Morris, 2010; Figure 7(c)). For the diffusional assisted grain-boundary sliding regime, the dissipation is controlled by stress concentrations near corners on the interface, with the energy dissipation at each corner dependent upon the angle subtended by the corner, and on the local orientation of the interface relative to the principal axes of applied stress. The dissipation was found to exhibit a power-law dependence on normalized frequency, that is, $Q^{-1} = A(\omega\tau_d)^{-\alpha}$. The power-law exponent α depends only upon the slope φ of the boundary, which determines the stress concentration at the grain corner. For a sawtooth boundary with $\varphi = 30^\circ$, $\alpha = 0.3$, comparable with experimental observations to be reviewed in Section 2.21.3.3.

Such micromechanical models of grain-boundary sliding provide a robust framework for the evaluation and assimilation of experimental data. The first significant indication, with increasing temperature, of the breakdown of strictly elastic behavior in fine-grained materials should be a broad dissipation peak with amplitude of order 10^{-2} and associated modulus dispersion, reflecting anelastic behavior associated with elastically accommodated grain-boundary sliding. With further increase in period and/or temperature, diffusion will become progressively more influential, allowing, firstly, additional

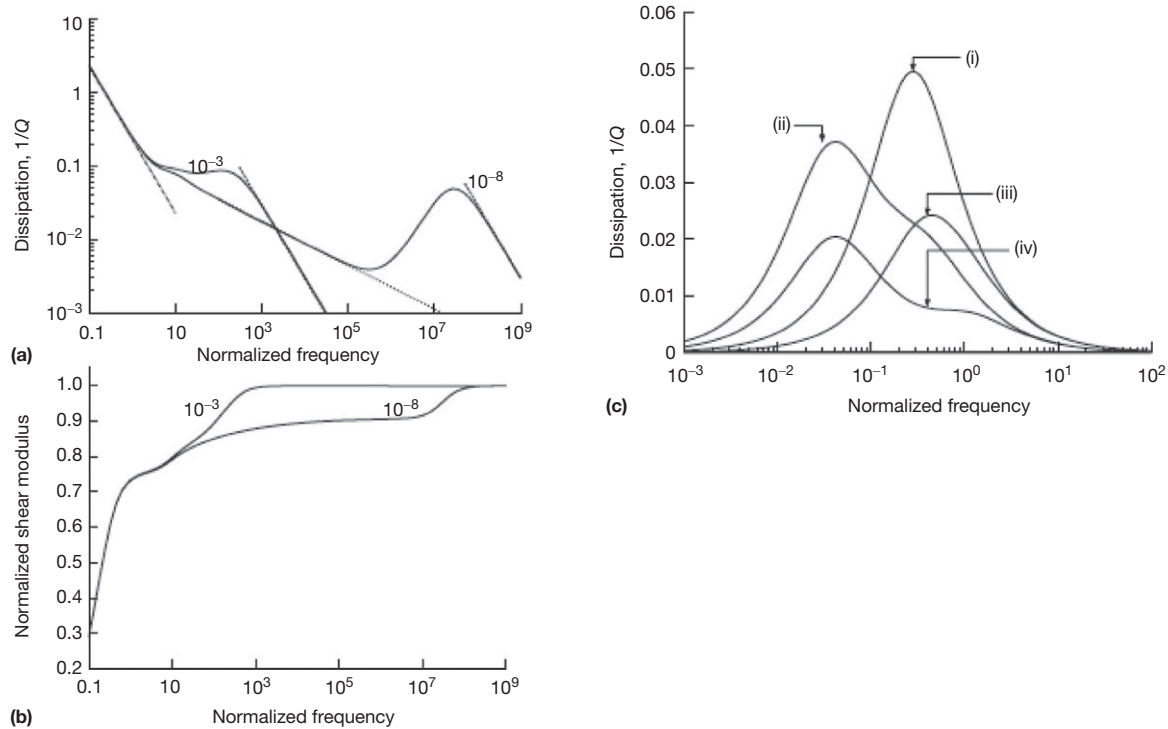


Figure 7 Dissipation (a) and shear modulus relaxation (b) calculated by Lee et al. (2011) for a $\varphi = 30^\circ$ sawtooth interface, with alternative values of $M = \tau_e/\tau_d$ of 10^{-8} and 10^{-3} . (c) The effect on Q^{-1} of spatial heterogeneity in grain size and/or viscosity (Lee and Morris, 2010, Figure 9). Curves labeled (i), (ii), (iii), and (iv) correspond, respectively, to uniform grain size and viscosity, tenfold variation of grain-boundary viscosity, fourfold variation of grain size, and both of the variations of (ii) and (iii). Reproduced from Jackson I, Faul UH, and Skelton R (2014) Elastically accommodated grain-boundary sliding: New insights from experiment and modeling. *Physics of the Earth and Planetary Interiors* 228: 2013–210, <http://dx.doi.org/10.1016/j.pepi.2013.11.014>, with permission.

anelastic strain within the diffusionally assisted sliding regime and, ultimately, the irrecoverable viscous strain of diffusionally accommodated grain-boundary sliding.

2.21.2.3.2.5 The effect of water on grain-boundary sliding

The influence of water on the viscoelastic relaxation associated with grain-boundary sliding has not yet been systematically studied experimentally. Exploratory forced-oscillation measurements on a hydrated dunite mylonite, encapsulated in platinum, and dehydrated *in situ*, revealed a pronounced reduction in shear modulus and increase in dissipation attributed mainly to the presence of a bulk aqueous fluid phase (Aizawa et al., 2008). Trace amounts of water dissolved as protonated defects in nominally anhydrous minerals such as olivine may significantly influence both intragranular viscoelastic relaxation (Section 2.21.2.2.2.7) and intergranular viscoelastic relaxation. In the latter context, Karato (2012) (see also Chapter 9.05) has argued that the characteristic time τ_e for the dissipation peak associated with elastically accommodated grain-boundary sliding should vary with water concentration C_w and temperature T as

$$\tau_e(T, C_w) \propto C_w^{-r} \exp(E/RT) \quad [63]$$

Concerning the exponent r , values between 1 and 2 were inferred from the water sensitivity of the large-strain rheology.

2.21.2.4 Relaxation Mechanisms Associated with Phase Transformations

2.21.2.4.1 Stress-induced variation of the proportions of coexisting phases

Relaxation associated with stress-induced change of the proportions of coexisting crystalline or solid and liquid phases has been analyzed in detail by Darinskiy and Levin (1968), Vaišnys (1968), and Jackson and Anderson (1970). The following simplified treatment is intended to explain the nature of such relaxation. Consider a region of pressure (P)–temperature (T)–bulk composition (X) space within which two phases such as a pair of low- and high-pressure polymorphs with density contrast $(\delta\rho/\rho)_0$ coexist in thermodynamic equilibrium. A superimposed small fluctuation p_s in pressure (under isothermal conditions), arising, for example, from a seismic compressional wave will induce changes in the equilibrium proportions and compositions of the coexisting phases. If the width of the two-phase region is δP (for given T and X), the magnitude of the implied fractional density perturbation is approximately

$$\varepsilon_a = (\delta\rho/\rho)_a = (p_s/\delta P)(\delta\rho/\rho)_0 \quad [64]$$

The volumetric strain specified by eqn [64] is proportional to the pressure perturbation, and the attainment of the perturbed equilibrium will require finite time for diffusional

rearrangement of the various chemical species. Moreover, the process is reversible on removal of the pressure perturbation. The conditions for anelastic behavior (identified in [Section 2.21.2.1.1](#)) are thus clearly satisfied. The corresponding elastic strain is given by

$$\varepsilon_e = (\delta\rho/\rho)_e = p_s/\underline{K} \quad [65]$$

where $\underline{K}(X, T)$ is the appropriate average of the unrelaxed bulk moduli for the coexisting phases. The relaxation strength, given by the ratio $\varepsilon_a/\varepsilon_e$ of the anelastic and elastic strains as in eqn [4], is thus

$$\Delta_v = (\underline{K}/\delta P)(\delta\rho/\rho)_0 \quad [66]$$

Under fully relaxed conditions, the total volumetric strain is the sum of the elastic and anelastic contributions, so that the relaxed bulk modulus K_R is given by

$$K_R^{-1} = (\delta\rho/\rho)/p_s = K_U^{-1}(1 + \Delta_v) \quad [67]$$

Because $\underline{K}/\delta P$ can be very large, Δ_v can be substantial (>1) even for a modest density contrast of order 0.01 ([Vaišnys, 1968](#)). The thermodynamic coexistence of the two phases, especially in subequal proportions near the middle of the two-phase loop, presumably means that nucleation is no barrier to further incremental transformation in either direction. An increase in the volume fraction of whichever phase is favored by the instantaneous value of the fluctuating hydrostatic pressure at the expense of the other phase would presumably be accomplished most readily by the migration normal to itself of the phase boundary across which grains of the two phases are in contact.

The specific geometry of a sphere of radius $r=sR_e$ of the minor phase embedded within a concentric spherical shell of outer radius R_e ($\sim$ half the grain size d) of the other phase, exposed to a sinusoidally time-varying external pressure $p_s \exp(i\omega t)$, has been analyzed in detail by [Ricard et al. \(2009\)](#). For simplicity, the two phases were considered to be elastically isotropic with the same unrelaxed elastic bulk and shear moduli K_U and G_U , respectively, but with a fractional difference in density $(\delta\rho/\rho)_0$. The purely radial deformation of the two-phase composite is obtained from the simultaneous solution of three equations describing, respectively, the continuity of normal stress across the pressurized external surface, the continuity of normal stress across the interphase interface, and the relationship between the radial velocity discontinuity at the interface and the reaction rate, related in turn to the perturbation (from equilibrium) in pressure at the interface (cf. [Morris, 2002](#)). The solution for the bulk modulus in this approximation is

$$K(\omega) = K_U + (K_i - K_U)/(1 + i\omega\tau) \quad [68]$$

with

$$K_i = K_U - s^3(K_U - K_R)(K_U + 4G_U/3)/(K_U s^3 + 4G_U/3)$$

and

$$\tau = (R_e s / 3CK_U)(K_U + 4G_U/3)/(K_U s^3 + 4G_U/3)$$

where C is a rate constant for the phase transformation ($\text{m s}^{-1} \text{Pa}^{-1}$) to be constrained by experimental observations of transformation kinetics ([Ricard et al., 2009](#)). Partial

relaxation of the bulk modulus toward K_i (rather than the lower value K_R) as $\omega \rightarrow 0$ reflects the influence of the elastic rigidity of the matrix in shielding the transforming core from the fluctuating pressure on timescales much shorter than the Maxwell relaxation time. The time constant τ for such partial relaxation of bulk modulus was estimated by [Ricard et al. \(also Li and Weidner, 2008\)](#) to fall within the seismic band.

The volumetric strain associated with the phase transformation driven by the pressure fluctuation, associated, for example, with a compressional seismic wave provides a clear expectation of partial relaxation of the bulk modulus. Given that a fluctuating shear stress involves no fluctuation of mean stress (or pressure), it is less obvious that a shear stress fluctuation would induce a change in the proportions of coexisting phases and hence partial relaxation of the shear modulus. However, [Ricard et al. \(2009\)](#) invoked nonhydrostatic thermodynamics (e.g., [Paterson, 1973](#)) to argue that the phase transformation is driven not by perturbations in pressure but by perturbations in normal stress acting across the interphase interface. For their model two-phase composite, the normal stress acting across the interface varies systematically with the orientation of the interface relative to an applied shear stress field, thereby promoting selective growth or resorption of the core phase. The result is a transformational component of the shear strain (cf. eqn [65]) and partial relaxation of the shear modulus for timescales similar to those for transformational relaxation of the bulk modulus.

These ideas are also applicable to stress-induced variations in the proportion of melt in partially molten material. In this case, the pressure perturbation p_s slightly modifies the solidus and liquidus temperatures by an amount

$$\delta T_s \sim (dT_m/dP)p_s \quad [69]$$

If δT_0 is the width of the melting interval, then the change to the melt fraction caused by the pressure fluctuation p_s is

$$\delta\phi \sim \delta T_s / \delta T_0 \quad [70]$$

which plays an analogous role to $p_s/\delta P$ in the foregoing analysis ([Jackson and Anderson, 1970](#); [Mavko, 1980](#); [Vaišnys, 1968](#)). Accordingly, partial relaxation of the bulk modulus is expected for partially molten material subject to fluctuating mean stress on sufficiently long timescales. However, any partial relaxation of the shear modulus driven by local spatial gradients in normal stress, as in the analysis by [Ricard et al. \(2009\)](#) and invoked by [Li and Weidner \(2013\)](#) for partially molten peridotite, would be viable only in the absence of melt redistribution between adjacent differentially stressed parts of the melt network, that is, within the saturated–isolated regime ([O’Connell and Budiansky, 1977](#); [Section 2.21.2.5](#)).

2.21.2.4.2 Stress-induced migration of transformational twin boundaries

Another possible mechanism of seismic wave attenuation and dispersion, with particular potential application to the Earth’s silicate perovskite-dominated lower mantle (and perhaps parts of the lithosphere), involves the stress-induced migration of boundaries between ferroelastic twins. The ABO_3 perovskite structure relevant to the lower mantle ([Chapter 2.03](#)), comprising a 3D corner-connected framework of cation-centered

BO₆ octahedra with larger A cations occupying the cage sites, displays an extraordinary versatility based on the systematic tilting and/or rotation of adjacent octahedra. In this way, the structure is not only able to accommodate cations that vary widely in size and charge but also able to respond flexibly to changing conditions of pressure and temperature. Thus, many perovskites cooled from high temperature undergo a series of displacive phase transformations to structures of progressively lower symmetry, each transition accompanied by the appearance of a spontaneous shear strain. The reduction of symmetry typically results in the formation of a microstructure composed of transformational twins with different orientations (relative to the lattice of the parent crystal) meeting in domain walls.

The nature of anelastic relaxation associated with the stress-induced motion of such domain walls has been explained (e.g., Carpenter and Zhang, 2011; Harrison and Redfern, 2002; Schaller et al., 2001) as follows. Under an applied stress, the free energy degeneracy between adjacent twin domains is removed resulting in a force acting on the domain wall. Thus, domain walls will tend to migrate so as to enlarge the domains of relatively low free energy at the expense of those of higher energy. The result is an additional nonelastic contribution to the macroscopic strain that is proportional to the product of the spontaneous strain, the density of domain walls, and the distance through which they move. Interactions between domain walls, between domain walls and associated defects, and between domain walls and the surface of a laboratory specimen result in a finite mobility or equivalently a characteristic timescale for their motion that is thermally activated. Moreover, the process of domain-wall migration is reversible on removal of the applied stress – meeting the final criterion for anelastic behavior discussed in Section 2.21.2.1.1.

2.21.2.5 Anelastic Relaxation Associated with Stress-Induced Fluid Flow

The presence within a rock of an intergranular fluid phase creates additional opportunities for anelastic relaxation. Well-developed theoretical models predict the dependence of elastic bulk and shear moduli and attenuation upon the volume fraction and viscosity η_f of the fluid and upon the nature of the grain-scale fluid distribution and the angular frequency ω of the applied stress field (Hammond and Humphreys, 2000a,b; Mavko, 1980; O'Connell and Budiansky, 1977; Schmeling, 1985; Walsh, 1968, 1969; see reviews by Jackson, 1991 and Chapter 11.03).

The model microstructure typically comprises a population of fluid-filled inclusions of specified shape (e.g., ellipsoids, grain-boundary films, or grain-edge tubes) and connectivity embedded within a (usually elastically isotropic) matrix, subject to an externally imposed stress field. As a consequence of the distortion of the matrix, each fluid inclusion is exposed to a particular state of stress. Depending upon the frequency of the applied stress, any one of four distinct fluid stress regimes may be encountered: glued, saturated–isolated, saturated–isobaric, and drained, listed here in order of decreasing frequency (O'Connell and Budiansky, 1977; Figure 8). The response to an externally imposed shear stress will be considered first. At sufficiently high frequencies, within the glued regime, the fluid is able to support a nonhydrostatic stress with an effective shear modulus $|G| = \omega\eta_f$

not substantially less than the matrix rigidity so that relative tangential displacement of neighboring grains is inhibited and the influence of the fluid is minimal. The saturated–isolated regime, where the fluid no longer supports shear stress but fluid pressure varies between (even adjacent) inclusions of different orientations, is encountered at somewhat lower frequencies. For still lower frequencies, fluid pressures are equilibrated by fluid flow between adjacent inclusions ('melt squirt,' Mavko and Nur, 1975) in the saturated–isobaric regime. Finally, at very low frequencies, drained conditions will apply for which no stress-induced perturbation of pore fluid pressure (relative to that in an external reservoir) can be sustained.

The transitions between the glued, saturated–isolated, and saturated–isobaric regimes are possible causes of dispersion and attenuation under the conditions of laboratory petrophysical experimentation and for seismic waves within the Earth's crust and its deeper interior. The transition from the glued regime to the saturated–isolated regime, in which the fluid no longer supports shear stress but undergoes no grain-scale flow, is formally identical to the process of elastically accommodated grain-boundary sliding reviewed in the preceding text. The grain-boundary fluid inclusion is simply identified with the boundary region of aspect ratio $\alpha_b = \delta/d$ and low viscosity η_b , and the relaxation time is given by eqn [60] rewritten in terms of α_b as

$$\tau_e = \gamma\eta_b/G_U\alpha_b \quad [71]$$

The relaxation time for fluid squirt between the triple-junction tubules characteristic of a nonwetting melt was estimated by Mavko (1980) as

$$\tau_{s,t} = 160\eta_m/K_m\alpha_t^2 \quad [72]$$

where $\alpha_t = 2R/d$ is the aspect ratio of the tubules (diameter/length), K_m is the bulk modulus of the melt, and η_m is the viscosity of the melt. The relaxation time for melt squirt between ellipsoidal inclusions was given by O'Connell and Budiansky (1977) as

$$\tau_{s,e} = 2\pi\eta_m/K_s\alpha_e^3 \quad [73]$$

where K_s is the bulk modulus of the solid and α_e the aspect ratio (width/length) of the ellipsoidal melt inclusions.

The characteristic timescale for each of these three processes of anelastic relaxation thus depends on the viscosity of the fluid phase (or grain-boundary material) as well as on the aspect ratio of the fluid inclusion or grain-boundary region of relatively low viscosity. The variations of relaxation time for representative ranges of aspect ratio and viscosity for each of the three processes are contoured in Figure 9. Each line is the locus of all combinations of aspect ratio and viscosity that yield a particular relaxation time. All combinations (α, η) that plot above (below) a contour corresponding to a given relaxation time τ are associated with unrelaxed (relaxed) behavior for oscillation period $T_o = \tau$. For a given mechanism to produce a relaxation peak centered within the teleseismic band (1–1000 s), it is therefore required that the relaxation time calculated as a function of aspect ratio and viscosity falls between the 1 and 1000 s contours indicated in Figure 9. An interpretation of dissipation data from laboratory experiments on melt-bearing fine-grained olivine polycrystals, based on Figure 9, is presented in Section 2.21.3.3.

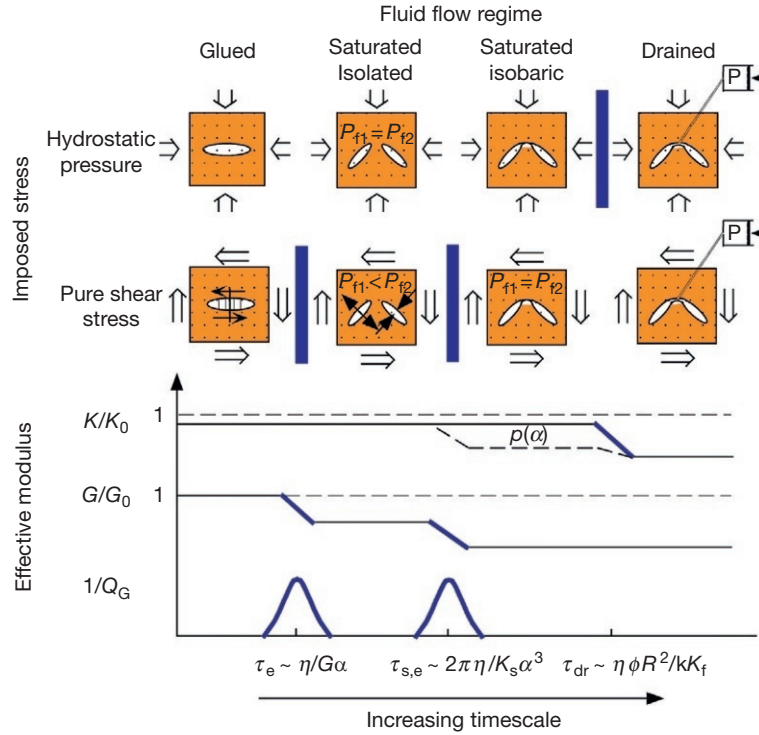


Figure 8 Fluid-flow regimes and effective elastic moduli for a medium containing ellipsoidal fluid inclusions of given aspect ratio α , as envisaged by O'Connell and Budiansky (1977). The upper row of panels shows the response of the medium to hydrostatic compression, whereas the lower row shows the response to shear. The vertical blue bars highlight the transitions between fluid-flow regimes that are expected to cause marked modulus relaxation. A distribution $p(\alpha)$ of fluid-inclusion aspect ratios leads to partial relaxation of the bulk modulus in the saturated–isobaric regime as indicated by the dashed line within the saturated–isobaric regime. P_{11} and P_{12} are the pore pressures in representative inclusions of different orientations relative to the applied stress. Adapted from Lu C and Jackson I (2006) Low-frequency seismic properties of thermally cracked and argon saturated granite. *Geophysics* 71: F147–F159.

The effective elastic moduli and hence relaxation strengths associated with the transitions between these fluid-flow regimes depend upon both the volume fraction ϕ and the aspect ratio α (minimum/maximum dimension) of the fluid inclusions. However, for relatively low fluid fractions and low aspect ratios (i.e., fluid-filled cracks rather than pores), the behavior is controlled primarily by a single variable known as crack density, ε (O'Connell and Budiansky, 1974). For a population of spheroidal inclusions of common low aspect ratio, ε is given by

$$\varepsilon = 3\phi/4\pi\alpha \quad [74]$$

whose definition can be generalized to accommodate a distribution of crack aspect ratios.

For the transition between the glued and saturated–isolated regimes, the fractional relaxation of the shear modulus is given, for low crack density ε , by

$$\begin{aligned} \delta G/G &\sim 32(1-\nu)\varepsilon/[15(2-\nu)] \\ &= (32/35)\varepsilon \quad (\text{for } \nu = 1/4) \end{aligned} \quad [75]$$

For the transition from the saturated–isolated regime to the saturated–isobaric regime, the further relaxation of the shear modulus is

$$\delta G/G \sim 32(1-\nu)\varepsilon/45 = (8/15)\varepsilon \quad (\text{for } \nu=1/4) \quad [76]$$

meaning that fluid squirt is only about half as effective as elastically accommodated grain-boundary sliding as a

relaxation mechanism (O'Connell and Budiansky, 1977). A nonwetting fluid, confined to grain-edge tubules, is much less effective in reducing the shear modulus in both saturated–isolated and saturated–isobaric regimes (Mavko, 1980).

As regards the bulk modulus, the presence of fluid inclusions with a bulk modulus K_f substantially lower than that (K_s) of the crystalline matrix will result in a modest reduction of the modulus for the drained regime given by

$$K \sim K_s[1 - (K_s/K_f)\phi] \quad [77]$$

(Hudson, 1981; O'Connell and Budiansky, 1974). In response to externally imposed changes in mean stress (Figure 8), fluid inclusions of common aspect ratio but different orientations experience the same perturbation in pore pressure – meaning that there is no distinction between the saturated–isolated and saturated–isobaric regimes. Given the existence of a distribution of fluid-inclusion aspect ratios $p(\alpha)$, however, stress-induced fluid flow will occur, for example, between cracks and pores, with associated partial relaxation of the bulk modulus (Budiansky and O'Connell, 1980; Figure 8). In a partially molten medium, the maintenance of equilibrium proportions of the coexisting crystalline and liquid phases results in a lower effective compressibility for the fluid phase on sufficiently long timescales and a large anelastic reduction in the bulk modulus as discussed in Section 2.21.2.4.1.

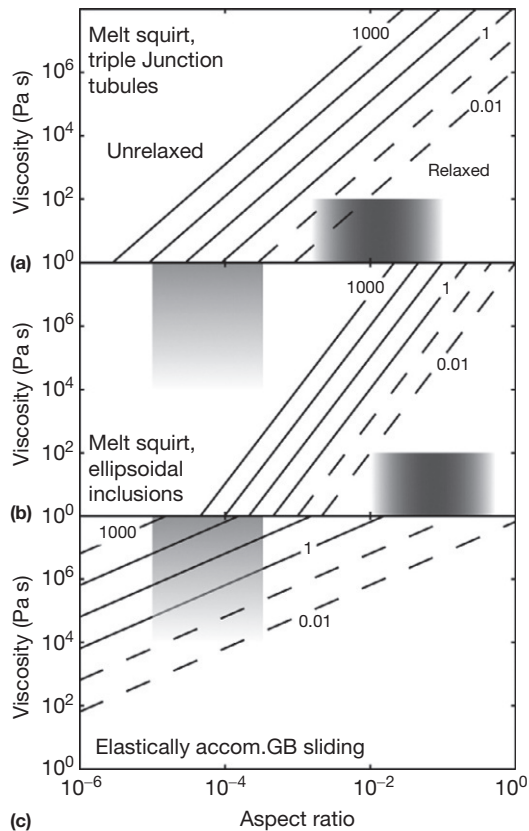


Figure 9 Relaxation times for elastically accommodated grain-boundary sliding and melt squirt as functions of the aspect ratio of the melt inclusion or grain-boundary region and of the melt or grain-boundary viscosity as described in the text. Values of the relevant elastic moduli, viscosities, and aspect ratios are appropriate for olivine–basalt system at 1200–1300 °C. After Schmeling (1985), from Faul et al. (2004) with permission.

2.21.3 Insights from Laboratory Studies of Geologic Materials

2.21.3.1 Dislocation Relaxation

2.21.3.1.1 Linearity and recoverability

Linearity of dislocation-controlled mechanical behavior requires that the dislocation density be independent of the applied stress and therefore that dislocation multiplication be avoided. For synthetic polycrystals of representative grain size 1–100 μm and Burgers vector of 0.5 nm, the critical elastic strain amplitudes for the onset of Frank–Read multiplication of the longest possible dislocation segments (with $L=d$), calculated from eqn [13], are 5×10^{-4} to 5×10^{-6} , respectively. These correspond (for $G=50$ GPa) to stresses of 25–0.25 MPa, respectively (see also Chapter 2.18). The linear regime is thus experimentally accessible over a wider range of stress and strain amplitudes in more fine-grained polycrystals (e.g., Gribb and Cooper, 1998a). The same argument applied to the larger grain sizes (1–10 mm) of the Earth’s upper mantle yields critical elastic strain amplitudes of 5×10^{-7} to 5×10^{-8} for the onset of dislocation multiplication and hence nonlinear behavior. Of course, the presence of impurities and other dislocations

means that dislocation segments will generally be substantially smaller than the grain size – expanding the field for linear behavior to larger strains.

Recoverability of the nonelastic strains associated with dislocation migration requires that dislocations remain firmly pinned by impurities or interactions with other dislocations. For a scenario ($E_{\text{up}} \sim 200\text{--}400$ kJ mol $^{-1}$, $a \sim b \sim 0.5$ nm and $L \sim 3\text{--}30$ μm) representative of silicate materials under laboratory or upper-mantle conditions, the critical stress for unpinning σ_{up} is predicted (eqn [51]) to be of order 0.1–1 MPa corresponding to shear strain amplitudes of order $10^{-6}\text{--}10^{-5}$. It follows that thermally assisted unpinning is likely to be encountered in laboratory internal friction experiments typically performed at strain amplitudes of $10^{-6}\text{--}10^{-4}$ (e.g., Karato and Spetzler, 1990; Nowick and Berry, 1972). Under these circumstances, one would expect more strongly frequency-dependent attenuation ($Q^{-1} \sim \omega^{-1}$ in the viscous regime; Figure 2) and possibly nonlinear behavior resulting from dislocation multiplication in the longer dislocation segments. Unpinning is less likely at the lower stresses and strains of teleseismic wave propagation ($<10^{-6}$, e.g., Shearer, 1999, p. 19).

2.21.3.1.2 Laboratory measurements on single crystals

Notwithstanding the potential importance of dislocation relaxation mechanisms in seismic wave attenuation, relevant laboratory experiments on geologic materials have been few and far between. Guéguen et al. (1989) tested both untreated and predeformed single crystals of forsterite in low-strain ($10^{-6}\text{--}10^{-5}$) torsional forced oscillation at periods of $10^{-3.5}\text{--}10$ Hz and temperatures as high as 1400 °C. The prior deformation was a compressive test at 1600 °C to 1% strain with the maximum principal stress (20 MPa) oriented parallel to $[111]_c$, which direction served also as the axis for the subsequent torsional oscillation tests. This choice of crystal orientation provides a satisfactory compromise that delivers substantial resolved shear stress for the dominant $[100](010)$ dislocation slip system in both the prior compressive deformation and subsequent torsional tests. The effect of the prior deformation was to substantially increase the average dislocation density from $\sim 10^{-3}$ to $\sim 10^{-1}$ μm^{-2} . For each specimen, the observed dissipation was dominated by an intense and broad absorption band (eqn [49]) with an activation energy $E=440 \pm 50$ kJ mol $^{-1}$ and exponent $\alpha=0.20 \pm 0.03$. A minor absorption peak superimposed upon the background was observed near 0.1 Hz. The dissipation increased markedly as the result of prior deformation, about fourfold at 1400° and 1000 s period (Figure 10, inset). Guéguen et al. argued plausibly that this observation, along with the similar activation energy for high-temperature dislocation creep in the same material, implicates relaxation associated with the stress-induced migration of the dominant $b=[100]$ edge dislocations. The similarly high activation energies for dislocation damping and creep have subsequently been interpreted by Karato (1998) to suggest a common reliance on the nucleation and migration of kink pairs (see succeeding paragraph).

Torsional forced-oscillation measurements, performed at low strain amplitudes ($\sim 10^{-6}$) and high temperatures (to 1500 K) on single-crystal MgO with an average dislocation density of about 5×10^{-3} μm^{-2} , are similarly well described

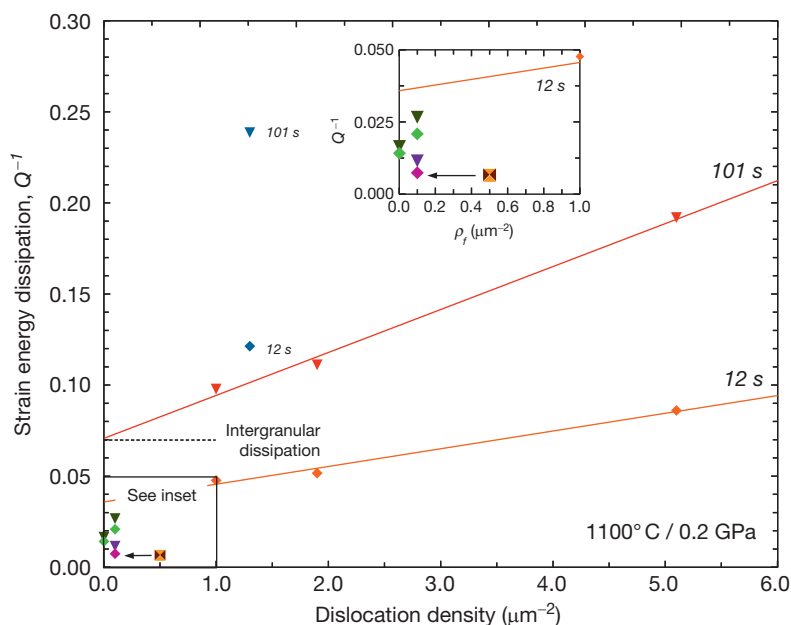


Figure 10 Dissipation data for polycrystalline olivine and single-crystal forsterite, tested undeformed and predeformed in torsional forced oscillation, plotted against dislocation density at 1100 °C, and for the polycrystalline olivine, 0.2 GPa confining pressure, for two representative oscillation periods: 12 and 101 s. The data for hot-pressed undeformed, and compressively predeformed, olivine (orange diamonds at 12 s period, and red inverted triangles at 101 s period) define the color-coded linear trends whose intercepts represent the inferred dissipation for the intergranular relaxation processes acting alone. The corresponding data for torsionally predeformed olivine are shown by the blue symbols. Results from forced-oscillation testing on single-crystal forsterite (undeformed and predeformed) are shown by the light and dark green symbols (Guéguen et al., 1989). The results of evaluating the Burgers-type model of Jackson and Faul (2010) at upper mantle grain sizes of 1 mm (purple inverted triangle for 101 s and magenta diamond for 12 s) and 10 mm (brown bow tie for 101 s and orange square for 12 s) are positioned for convenience at $\rho \sim 0.1 \mu\text{m}^{-2}$ (see inset). Adapted from Farla RJM, Jackson I, Fitz Gerald JD, Faul UH, and Zimmerman ME (2012a) Dislocation damping and anisotropic seismic wave attenuation in Earth's upper mantle. *Science* 336: 332–335.

by eqn [49] with $E = 230 \text{ kJ mol}^{-1}$ and $\alpha = 0.30$ (Getting et al., 1997). The much lower activation energy for dislocation damping than for dislocation creep (400 kJ mol^{-1} ; Hensler and Cullen, 1968) led Karato (1998) to suggest that geometric kink migration might account for the dislocation damping with nucleation and migration of kink pairs responsible for the dislocation creep.

2.21.3.1.3 Laboratory measurements on natural rocks and synthetic polycrystals

Absorption band behavior probably attributable at least in part to dislocation damping also dominates the high-temperature internal friction measured on relatively coarse-grained rocks (Berckheimer et al., 1982; Jackson et al., 1992; Kampmann and Berckheimer, 1985). Activation energies for dissipation are generally comparable to those for creep – consistent with Karato's interpretation of the Guéguen et al. data for single-crystal forsterite. None of these studies involved a systematic examination of dislocation microstructure, and the shear moduli measured (at ambient pressure) in Berckheimer's laboratory were inevitably significantly compromised by thermal microcracking.

More recently, Farla et al. (2012a) reported results for two suites of relatively fine-grained olivine polycrystals, hot-pressed from fully synthetic (sol-gel) precursor powders or

from pulverized handpicked natural (San Carlos, Arizona) olivine crystals, respectively. For each suite of polycrystals, torsional forced-oscillation tests were performed over restricted ranges of temperature intended to minimize *in situ* dislocation recovery (Farla et al., 2011) both on (undeformed) hot-pressed specimens and on selected specimens predeformed by dislocation creep in either axial compression or torsion. Systematically enhanced dissipation with increasing dislocation density was associated with prior deformation – suggestive of a contribution from stress-induced dislocation relaxation (Figure 10). More intense dissipation for a given dislocation density, for specimens predeformed in torsion, is attributed to generally more favorable orientation of dislocations for reactivation for glide during subsequent low-stress testing in the same torsional geometry.

2.21.3.2 Stress-Induced Migration of Transformational Twin Boundaries in Ferroelastic Perovskites

Harrison and his colleagues have reported the results of a thorough study of the anelastic behavior associated with the stress-induced motion of domain walls in single crystals of the ferroelastic perovskite LaAlO_3 (Harrison and Redfern, 2002; Harrison et al., 2004). They combined three-point bending experiments performed under combined steady and oscillating

load with *in situ* optical observations of the domain-wall motions. Essentially elastic behavior was observed for temperatures $T > T_c$ within the stability field of the high-symmetry phase (T_c is the phase transformation temperature). Strongly anelastic behavior, involving both a sharp dissipation peak centered on T_c and distributed dissipation within the stability field of the low-symmetry ferroelastic phase, is associated with the thermally activated motion of the domain walls separating transformational twins formed spontaneously on cooling below T_c . At sufficiently low temperatures, domain-wall mobility is reduced to such an extent that the domain microstructure is frozen and elastic behavior with a high unrelaxed modulus prevails. The transition between the frozen and ferroelastic regimes is associated with pronounced relaxation ($\delta Y/Y \sim 0.9$) of Young's modulus Y and an associated dissipation peak of amplitude ($\tan \delta = Q^{-1} \sim 1$). The dissipation peak is somewhat broader than the Debye peak of the standard anelastic solid and was modeled by Harrison and Redfern (2002) with a Gaussian distribution of activation energies suggestive of pinning of domain walls by oxygen vacancies.

Subsequent studies on a number of additional ferroelastic perovskites offer further insight into the nature of domain-wall mobility and associated anelastic relaxation. The review by Carpenter and Zhang (2011) highlights the likelihood that alternative modes of domain-wall motion operate at different frequencies and levels of stress. These include the advance/retreat of the tips of needle-shaped twin domains, the reversible bowing of pinned segments of twin walls, and the macroscopic migration of twin boundaries. The dynamics of such processes of twin boundary migration have recently been modeled by Salje et al. (2013) with molecular dynamic techniques. The fact that twin boundaries are mobile in some low-symmetry perovskites and not in others is associated by Carpenter and Zhang (2011) with widely different activation energies for domain-wall migration. More specifically, it has been suggested that domain-wall mobility may be restricted to phases with positive volume strain relative to the cubic parent and thick domain walls (Daraktchiev et al., 2006).

2.21.3.3 Grain-Boundary Relaxation Processes

2.21.3.3.1 Grain-boundary migration in b.c.c. and f.c.c. Fe

Like many other metals, the low-temperature b.c.c. polymorph of iron was studied with resonant (pendulum) techniques in the early days of internal friction studies. More recently, Jackson et al. (2000) employed subresonant forced-oscillation methods to probe the viscoelastic behavior of mildly impure polycrystalline iron over an extended temperature range reaching well into the stability field of the high-temperature f.c.c. phase.

Markedly viscoelastic behavior, dominated by the monotonically frequency- and temperature-dependent 'high-temperature background,' was observed within each of the b.c.c. and f.c.c. stability fields for both mild steel and soft iron compositions. The behavior of the b.c.c. phase is adequately described by eqn [49] with an activation energy of $E = 280(30)$ kJ mol⁻¹ not very different from that for lattice diffusion (239 kJ mol⁻¹; Frost and Ashby, 1982) and $\alpha = 0.20(2)$. For the f.c.c. phase, α determined during staged cooling from 1300 °C to 800 °C typically assumes values of 0.2–0.3 at the

highest and lowest temperatures within this range but reaches significantly lower values ~ 0.1 at intermediate temperatures. The result is a poorly defined Q^{-1} plateau at short periods and 900–1100 °C, suggestive of a broad Q^{-1} peak superimposed upon the background (Jackson et al., 2000, Figure 8(b)).

Each of these phases displays unusually strong elastic anisotropy at elevated temperatures and ambient pressure: G_{RS}/G_{HS} decreases from 0.91 to 0.61 between 20 and 900 °C for b.c.c. Fe (Dever, 1972), whereas the only available single-crystal elasticity data for f.c.c. Fe yield $G_{RS}/G_{HS} = 0.74(1)$ at 1155 °C. Relaxation of the initially inhomogeneous stress field toward the Reuss state of uniform stress by grain-boundary migration, first suggested by Leak (1961), is accordingly a potentially important relaxation mechanism in polycrystalline iron that is worthy of more detailed investigation.

2.21.3.3.2 Grain-boundary sliding in melt-free materials

The high-temperature behavior of fine-grained synthetic rocks (and analogous ceramic materials) has been the focus of a substantial body of recent work. Fine-grained ultramafic materials with or without a small melt fraction have been made by hot-isostatic pressing of powders prepared by crushing natural dunites or olivine crystal separates or by a sol-gel procedure (Gribb and Cooper, 1998a, 2000; Jackson et al., 2002, 2004; Tan et al., 1997, 2001; Xu et al., 2004). These studies have consistently revealed broad absorption band behavior. Pronounced superimposed dissipation peaks were reported only in the studies of Jackson et al. (2004) and Xu et al. (2004) of melt-bearing materials.

Of these materials, only the olivine polycrystals, prepared from handpicked natural olivine crystals or sol-gel precursors, are pure enough to remain essentially melt-free during testing by high-temperature mechanical spectroscopy (Jackson et al., 2002; see also Jackson et al., 2004). The reconstituted dunite tested by Gribb and Cooper (1998a) is only nominally melt-free – the usual inventory of impurities being expected to produce 0.1–1% melt at temperatures of 1200–1300 °C. Previously, it was concluded that the results for essentially melt-free olivines depart markedly from the prescriptions of the widely used Raj–Ashby model of elastically and diffusively accommodated grain-boundary sliding. Despite intensive sampling of the transition from elastic behavior through essentially anelastic to substantially viscous deformation, dissipation peaks attributable to elastically accommodated grain-boundary sliding are conspicuous by their absence. Instead, it was observed that the dissipation apparently increases monotonically with increasing oscillation period and temperature in the manner of the high-temperature background. Also, the variation with oscillation period and grain size, reported as $Q^{-1} \sim (T_0/d)^{1/4}$, is much milder than predicted for the diffusional creep transient (eqn [61]). For other ceramic systems lacking a widely distributed grain-boundary phase of low viscosity, 'grain-boundary' Q^{-1} peaks are similarly absent or very broad and of subsidiary significance relative to the background dissipation (Lakki et al., 1999; Pezzotti et al., 1998; Webb et al., 1999).

However, guided by the results of recent micromechanical modeling (Lee and Morris, 2010; Lee et al., 2011; Morris and Jackson, 2009) summarized in Section 2.21.2.3.2.4, Jackson and Faul (2010) made a further attempt to reconcile the theory

of grain-boundary sliding with the growing forced-oscillation dataset for fine-grained, essentially melt-free polycrystalline olivine. These data, reprocessed to correct for interfacial compliance as suggested by Jackson et al. (2009), were first fitted by nonlinear least squares to a generalized Burgers model (eqn [4]) with a distribution $D(\tau)$ of anelastic relaxation times appropriate for the monotonic high-temperature background dissipation, that is,

$$D_B(\tau) = \alpha \tau^{\alpha-1} / (\tau_H^\alpha - \tau_L^\alpha) \quad [78]$$

with $0 < \alpha < 1$ for $\tau_L < \tau < \tau_H$ and zero elsewhere (Minster and Anderson, 1981). However, comparison of the optimal model of this type with the experimental data revealed some misfit associated with a possible dissipation plateau at temperatures below 1000 °C and a deficit of about 7% in unrelaxed modulus, relative to the well-established high-frequency (anharmonic) value. These observations provided the motivation for tentative inclusion in the model of a dissipation peak superimposed upon the monotonic background, along with the associated dispersion. For this purpose, the distribution of anelastic relaxation times specified by eqn [78] was augmented by the separately normalized distribution (Jackson, 2005; Kampfmann and Berckhemer, 1985)

$$D_P(\ln \tau) = \sigma^{-1} (2\pi)^{-1/2} \exp \left\{ -[\ln(\tau/\tau_P)/\sigma]^2 / 2 \right\} \quad [79]$$

with relaxation strength Δ_P . The lower (τ_L) and upper (τ_H) limits for the distribution of 'background' anelastic relaxation times, the 'peak' anelastic relaxation time τ_P , and the Maxwell viscous relaxation time $\tau_M = \eta/\mu$, are each subject to power-law dependence on grain size and an Arrhenian variation with temperature (and pressure) through an activation enthalpy (with $E = 360(6) \text{ kJ mol}^{-1}$ and $V = 10 \text{ cm}^3 \text{ mol}^{-1}$). Different values are allowed for the grain-size exponents for anelastic (optimal $m_a = 1.31(4)$ for $i = L, H, P$) and viscous relaxation (m_v fixed at three for $i = M$). The preferred 'background+peak' model is compared with the constraining forced-oscillation data in Figure 11. The exponent $\alpha = 0.27(1)$ in $D_B(\tau)$ accounts for the power-law variation of dissipation with period (with similar exponent) at moderate to high temperatures. The impact of the broad, low-amplitude dissipation peak ($\Delta_P = 0.057(2)$ with σ fixed at 4) is seen at temperatures below 1000 °C in the plateau at $Q^{-1} \sim 0.01$. A recent reanalysis of the same information by Olugboji et al. (2013) using a grid search method yields similar values for the model parameters, including confirmation that the value of σ cannot be constrained by these data.

Such modification of the distribution $D(\tau)$ of anelastic relaxation times to include a dissipation peak and associated modulus dispersion, plausibly associated with previously unrecognized elastically accommodated grain-boundary sliding, thus provides a seamless transition between elastic, anelastic, and viscous behaviors that accord with the predictions of the latest micromechanical modeling. Further tantalizing, but still inconclusive, evidence for the presence of this dissipation peak has recently been reported in studies of an olivine polycrystal enclosed within a copper rather than steel jacket and accordingly free from the masking effects of the austenite-ferrite phase transformation (Jackson et al., 2014). Complementary torsional microcreep tests indicate that the

nonelastic strains for timescales of 1–1000 s are mainly recoverable (i.e., anelastic) – consistent with substantial contributions from elastically accommodated and diffusively assisted grain-boundary sliding.

Finally, as previously mentioned in Section 2.21.3.1.3, Farla et al. (2012a,b) recently measured dislocation densities $\sim 1 \mu\text{m}^{-2}$ for such hot-pressed polycrystals, raising the possibility that the mild grain-size sensitivity ($m_a = 1.31$) of the anelastic relaxation times is attributable in part to the existence of a grain size-insensitive contribution from dislocation relaxation.

2.21.3.3.3 Melt-related viscoelastic relaxation

In the presence of small basaltic melt fractions ranging from 10^{-4} to 4×10^{-2} , qualitatively different behavior has been observed in the form of a broad dissipation peak superimposed upon a dissipation background enhanced relative to that for melt-free material of the same grain size (Jackson et al., 2004; Figure 12). The peak width exceeds that of the Debye peak of the standard anelastic solid by about two decades in period and is independent of temperature but varies mildly with the breadth of the grain-size distribution. The peak height is well described by power-law dependence upon maximum melt fraction. The peak position (period) varies exponentially with $1/T$ (with a high activation energy E_P of 720 kJ mol^{-1} – possibly reflecting both thermal and compositional influences upon viscosity) and linearly with grain size. This grain-size sensitivity is that expected of elastically accommodated grain-boundary sliding (eqn [60]). These observations have been compared and contrasted with the somewhat different findings of Gribb and Cooper (2000) and Xu et al. (2004) by Faul et al. (2004).

It has long been understood that the viscoelastic relaxation associated with partial melting should depend upon the extent to which the melt wets the grain boundaries (e.g., Stocker and Gordon, 1975). It had long been the conventional wisdom that basaltic melt in textural equilibrium does not normally wet olivine grain faces – being confined instead to a network of interconnected grain-edge tubules of cusped triangular cross section (e.g., von Bargen and Waff, 1986; Chapter 2.18). However, in addition to the network of grain-edge tubules, Faul et al. (1994) identified a population of larger localized melt pockets. Among the melt-bearing olivine polycrystals described by Faul et al. (2004), for example, the melt fraction ranges widely from $\sim 10^{-4}$ to 4×10^{-2} with aspect ratios of 3×10^{-3} to 10^{-1} for grain-edge tubules and 10^{-2} to 5×10^{-1} for the isolated melt pockets. For such aspect ratios and the bulk melt viscosities of 1–100 Pa s appropriate for 1200–1300 °C, melt squirt, whether between adjacent tubules or between adjacent melt pockets, is expected at timescales substantially shorter than seismic periods (Figure 9(a) and 9(b)) in accord with the results of previous analyses (Hammond and Humphreys, 2000a; Schmeling, 1985). Moreover, the relaxation strength for squirt flow between melt tubules is low (Mavko, 1980): ~ 0.02 corresponding to a Q^{-1} peak height of only 0.01 for a melt fraction ϕ of 0.04. For these and other reasons given by Faul et al. (2004), melt squirt was rejected as a viable explanation for the melt-related dissipation peak. Instead, it was argued that elastically accommodated grain-boundary sliding involving boundary regions of aspect ratio

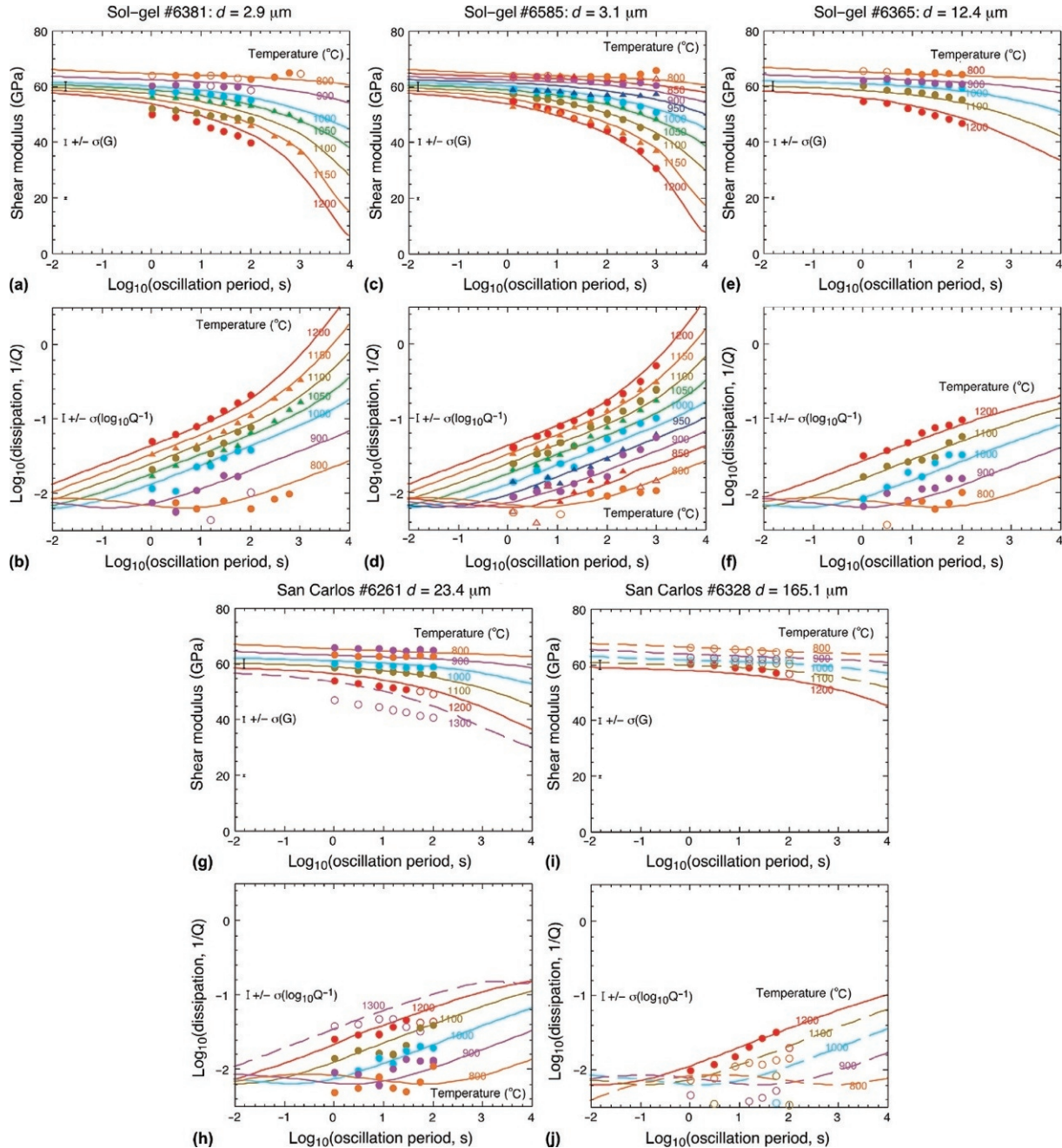


Figure 11 Comparison between forced-oscillation data (plotting symbols) and the optimal, grain size-sensitive, background + peak Burgers model (curves) fitted to 204 (G, Q^{-1}) data pairs for essentially melt-free sol-gel-derived olivine polycrystals 6381, 6585, and 6365 and San Carlos-derived olivine polycrystals 6261 and 6328 ranging in mean grain size from 2.9 μm in the top left to 165.1 μm in the lower right, as indicated. Solid symbols identify the subset of data used to constrain the model. The uncertainties in shear modulus ($\sigma(G)/G = 0.03$) and dissipation ($\sigma(\log_{10} Q^{-1}) = 0.05$) are indicated by the error bars on the left-hand side of each panel. Reproduced from Jackson I and Faul UH (2010) Grainsize-sensitive viscoelastic relaxation in olivine: Towards a robust laboratory-based model for seismological application. *Physics of the Earth and Planetary Interiors* 183: 151–163, with permission.

$\sim 10^{-4}$ has the potential to contribute to attenuation at seismic frequencies – provided that the effective grain-boundary viscosity is, not unreasonably, 10^4 – 10^9 Pa s for temperatures of 1300–1000 °C (Figure 9(c)).

Two new findings suggest that this interpretation of the melt-related dissipation peak must now be revisited. The first

is the previously discussed evidence for a small and broad dissipation peak, superimposed at temperatures of 800–900 °C and seismic frequencies, upon the background dissipation in melt-free materials, and attributed to elastically accommodated grain-boundary sliding. The second argument concerns emerging recognition of the role of melt films in the

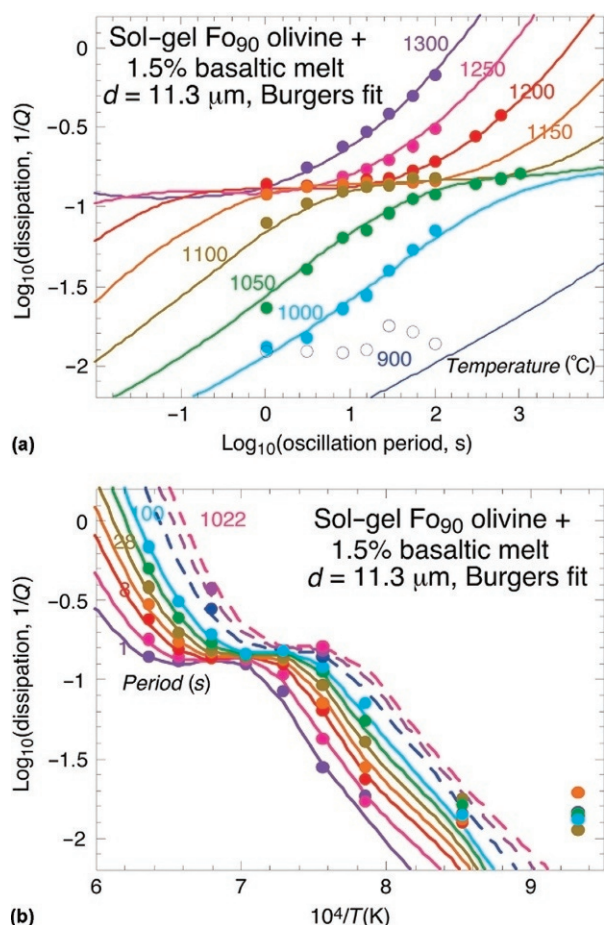


Figure 12 $\log(Q^{-1})$ versus (a) $\log(\text{oscillation period})$ and (b) reciprocal temperature for a representative melt-bearing polycrystal, displaying a broad dissipation peak superimposed upon the monotonic high-temperature background. Adapted from Jackson I, Faul UH, Fitz Gerald J, and Tan BH (2004) Shear-wave attenuation and dispersion in melt-bearing olivine polycrystals. Part I: Specimen fabrication and mechanical testing. *Journal of Geophysical Research* 109, <http://dx.doi.org/B0620110.1029/2003JB0002406>, with data corrected for interfacial compliance (Jackson et al., 2009).

grain-scale melt distribution in peridotitic rocks (Cmíral et al., 1998; Garajčić et al., 2013). In the latter serial-sectioning study, it was shown that grain boundaries in olivine polycrystals containing basaltic melt fractions of 0.016 and 0.036, respectively, are commonly wetted by melt films of thickness 10–100 nm and aspect ratio 10^{-4} – 10^{-3} . Such low aspect ratios, combined with normal basaltic melt viscosities of 1–100 Pa s, yield squirt relaxation times in the seismic-frequency band (Figure 9(b)). This new attribution of the melt-related dissipation peak and associated modulus dispersion to melt squirt requires further testing with a combination of torsional and newly developed flexural oscillation methods (Jackson et al., 2011). The latter have the potential to provide additional constraints on the timescales for stress-induced melt redistribution.

Broadly similar observations have been made for polycrystalline MgO. Dense polycrystals of high purity display only a monotonically frequency- and temperature-dependent Q^{-1}

background and associated dispersion of the shear modulus (Barnhoorn et al., 2007). In marked contrast, a previous study of MgO of lower purity (Webb and Jackson, 2003) revealed a pronounced dissipation peak, superimposed upon the background and now tentatively attributed to the stress-induced redistribution of a grain-boundary phase of low viscosity. Further examples of both types of high-temperature viscoelastic behavior are provided by the fine-grained polycrystalline titanate perovskites studied as analogs for the high-pressure silicate perovskites by Webb et al. (1999). The purest and microstructurally simplest of these specimens was a SrTiO_3 specimen of $5 \mu\text{m}$ grain size. Its grains are untwinned and its essentially impurity-free grain boundaries meet in grain-edge triple junctions invariably $< 20 \text{ nm}$ in cross-sectional dimension. The lack of an extensive network of substantial grain-edge triple-junction tubules is reflected in background-only dissipation generally well described for temperatures between 900 and 1300 °C by eqn [49]. On the other hand, the CaTiO_3 specimens of 3 and $20 \mu\text{m}$ grain size are pervasively twinned and contain a significant level of silicate impurity responsible for well-developed networks of grain-edge tubules of cusped triangular cross section. With the benefit of hindsight, deviations from power-law fits to the $Q^{-1}(T_0)$ data at 1000 and 1050 °C (Webb et al., 1999, Table 4 and Figure 13) for the $20 \mu\text{m}$ specimen are consistent with the presence of a broad dissipation peak analogous to those characteristic of melt-bearing olivine and perhaps similarly interpretable in terms of melt squirt. For the more fine-grained CaTiO_3 specimen, any such peak may be masked by the relatively low-temperature onset of markedly viscous behavior.

2.21.3.4 Viscoelastic Relaxation in Cracked and Water-Saturated Crystalline Rocks

The sparse experimental observations concerning the effect of water saturation on the elastic moduli of cracked crystalline rocks of relatively low porosity, assembled by Lu and Jackson (2006), are reproduced in Figure 13. The existence of a mechanical relaxation spectrum first suggested by Gordon (1974) is confirmed by this more recent compilation. Ultrasonic, resonance, and forced-oscillation methods together allow more than eight decades' variation of period or frequency. The fractional change in elastic wave speed $\delta V_i/V_i$ that results from water saturation (with $P_f=0$) is plotted for the compressional ($i=P$), shear ($i=S$), and extensional ($i=Y$) bar modes. For microsecond to millisecond periods, the wave speeds are consistently increased by water saturation, the effect being more pronounced for compressional and extensional modes than in shear. The sign is reversed for periods greater than $\sim 0.1 \text{ s}$ with significant negative perturbations to both extensional and shear wave speeds for the 10–100 s periods of forced-oscillation methods.

Interpretation of the broad trend evident in Figure 13 requires estimates of the characteristic times for the various fluid-related relaxation mechanisms discussed in Section 2.21.2, for the special case of water saturation of cracks of aspect ratio $\sim 10^{-3}$. For relaxation of shear stress within an individual grain-scale fluid inclusion, eqn [71] predicts $\tau_e \sim \eta_d/G_u \alpha \sim 10^{-11} \text{ s}$; for squirt between adjacent cracks, eqn [73] yields $\tau_{s,e} = 2\pi\eta_d/K_s \alpha_e^3 \sim 10^{-4} \text{ s}$; and for the draining of a cm-sized laboratory rock

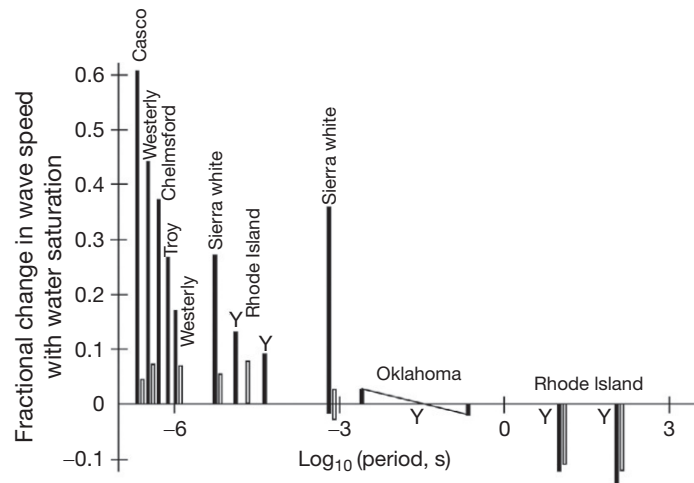


Figure 13 The effect of water saturation of granite (with zero pressure and confining pressure) on the speed of compressional (unlabeled solid bars), bar-mode longitudinal (solid bars labeled 'Y'), and shear waves (unfilled bars). The sources of the data for the various granite specimens (named after their provenance) are given by [Lu and Jackson \(2006, Figure 11\)](#) after which this figure has been redrawn.

specimen of porosity $\phi \sim 0.01$ and permeability $\sim 10^{-18} \text{ m}^2$, $\tau_{\text{dr}} = \eta \phi R^2 / k K_f \sim 10^{-1} \text{ s}$ ([Lu and Jackson, 2006](#)). Accordingly, [Lu and Jackson \(2006\)](#) concluded that the ultrasonic measurements at periods $< 10^{-5} \text{ s}$ probe the saturated–isolated regime, whereas near-zero values of $\delta G/G$, and hence $\delta V_s/V_s$, at the ms periods of resonance techniques are characteristic of the saturated–isobaric regime. Near-zero values of $\delta K/K$ for periods $> 10^{-3} \text{ s}$ are indicative of the drained regime. Chemical effects of water saturation, such as an increase in crack density and reduction in the stiffness of grain contacts, are required to explain the negative values of $\delta V/V$ in experimental data obtained at periods $> 0.01 \text{ s}$ ([Lu and Jackson, 2006](#)).

Recent broadband studies of water-saturated rocks employing both ultrasonic wave-propagation and forced-oscillation methods provide additional insight into the dispersion associated with squirt flow. Long-period (100 s) oscillating-pressure tests on an Icelandic basalt containing both cracks and pores yielded a substantially lower bulk modulus than ultrasonic wave speed measurements (10^{-6} s) – the difference being attributed to squirt flow between cracks and pores in the oscillating-pressure tests ([Adelinet et al., 2010](#)). In a study of a thermally cracked quartzite, [Schijns et al. \(2012\)](#) showed that water saturation results in a dramatic increase of elastic wave speeds measured at microsecond period, whereas the corresponding moduli were insensitive to water saturation at the much longer periods ($> 1 \text{ s}$) of forced-oscillation experiments. Moreover, [Adelinet et al. \(2010\)](#) measured a lower bulk modulus on the Icelandic basalt under drained, water-saturated conditions than for dry conditions – suggestive of a role for adsorbed water in increasing the compliance of grain contacts.

2.21.4 Geophysical Implications

2.21.4.1 Dislocation Relaxation

2.21.4.1.1 Vibrating-string model

The possibility that viscoelastic relaxation associated with the stress-induced motion of dislocations might explain the

attenuation and dispersion of seismic waves, especially in the Earth's upper mantle, has been widely canvassed ([Guéguen and Mercier, 1973](#); [Karato, 1998](#); [Karato and Spetzler, 1990](#); [Minster and Anderson, 1981](#)). [Guéguen and Mercier \(1973\)](#) invoked the vibrating-string model of dislocation motion as an explanation for the upper-mantle zone of low wave speeds and high attenuation. They associated an intragranular dislocation network with any observable high-temperature relaxation peak and suggested that a grain-boundary network of more closely spaced dislocations might explain the high-temperature background attenuation. It was suggested that impurity control of dislocation mobility might yield relaxation times appropriate for the seismic-frequency band.

A more ambitious attempt to produce a model of dislocation-controlled rheology consistent with both seismic wave attenuation and the long-term deformation of the mantle was made by [Minster and Anderson \(1981\)](#). They envisaged a microstructure established by dislocation creep in response to the prevailing tectonic stress σ_t and comprising subgrains of dimension L

$$\underline{L} = \gamma_s G b / \sigma_t = \gamma_s L_c \quad [80]$$

with a mobile dislocation density

$$A_m = \gamma (\sigma_t / G b)^2 = \gamma L_c^{-2} \quad [81]$$

where $L_c = G b / \sigma_t$ is the critical dislocation link length for multiplication by the Frank–Read mechanism (see discussion following eqn [12], and [Chapter 2.18](#)). From laboratory experiments on olivine ([Durham et al., 1977](#)), it was estimated that $\gamma_s \sim 20$ for well-annealed mantle olivine; γ is a constant of order unity ([Frost and Ashby, 1982](#)). Furthermore, it was argued that the distribution of dislocation segment lengths will be dominated by those of length

$$L \sim (5/3) L_c \quad [82]$$

for which the dislocation multiplication time, calculated with a migration velocity given by eqn [14], is a minimum. It follows from eqns [80]–[82] that the dislocation density within the

subgrains is essentially that (L^{-2}) of the Frank network with dislocation relaxation strength $\Delta \sim 0.1$ (eqn [23]). For $\sigma_t \sim 1$ MPa (strain rate of 10^{-15} s^{-1} with effective viscosity of 10^{21} Pa s), $L_c \sim 30 \text{ }\mu\text{m}$ and $A_m \sim 10^{-3} \text{ }\mu\text{m}^{-2}$. It was suggested that the total dislocation density should be much higher – being dominated by dislocations organized into the subgrain walls. The climb-controlled motion of these latter dislocations was invoked to explain deformation at tectonic stresses and timescales (Minster and Anderson, 1981).

Their suggestion of a dominant link length disallows an absorption band based on a wide distribution of segment lengths (eqn [50]). Minster and Anderson (1981) suggested instead that the seismic absorption band reflects a spectrum of activation energies. A frequency-independent upper-mantle Q^{-1} of 0.025 was shown to require a range δE of about 80 kJ mol^{-1} and to produce an absorption band only two to three decades wide.

A unified dislocation-based model for both seismic wave attenuation and the tectonic deformation of the Earth's mantle has been sought more recently by Karato and Spetzler (1990) and Karato (1998). Karato and Spetzler (1990) emphasized the apparent paradox whereby a Maxwell model based on reasonable steady-state viscosities seriously underestimates the level of seismic wave attenuation (their Figure 3). Equally, a transient-creep description of seismic wave attenuation extrapolated to tectonic timescales (Jeffreys, 1976) seriously overestimates the mantle viscosity. For a unified dislocation-based model, it is thus required that dislocations have much greater mobility (velocity/stress) at seismic frequencies than for tectonic timescales. Karato and Spetzler's assessment of relaxation strengths and relaxation times, based on the vibrating-string model of dislocation motion (eqn [23]) and revisited with a somewhat higher dislocation density of $10^{-3} \text{ }\mu\text{m}^{-2}$ (eqn [81]) applied to the upper mantle as in the preceding paragraph, is in general accord with that of Minster and Anderson. In particular, reasonable levels of seismic wave attenuation ($10^{-1} > \Delta > 10^{-3}$) would require segment lengths L of 1–10 μm , and a specific range of dislocation mobilities (b/B in eqn [14]) would be needed for relaxation times in the seismic band (Karato and Spetzler, 1990, Figure 7). The issue in all such analyses is to relate key parameters controlling Δ , τ , and indeed the steady-state effective viscosity η , to the intrinsic and/or extrinsic properties of dislocations, as appropriate. Karato and Spetzler noted that dislocation mobility is expected to increase with increasing temperature and water content but to decrease with increasing pressure. The segment length L for the vibrating-string model was shown to depend in different ways on the tectonic stress according to whether pinning is effected by interaction with impurities or other dislocations.

2.21.4.1.2 Kink model

The feasibility of seismic wave attenuation resulting from the stress-induced migration of kinks was also briefly explored by Karato and Spetzler (1990) and analyzed in more detail by Karato (1998). In the latter study, Karato identified three distinct stages of dislocation relaxation to be expected with progressively increasing temperature or stress and/or decreasing frequency. Stage I involves the reversible migration of pre-existing geometric kinks along Peierls valleys with characteristic timescale and relaxation strength given by eqns [27] and

[28]. The maximum anelastic strain resulting from migration of geometric kinks (eqn [30]) is of order 10^{-6} for a Frank network of dislocations with $\Delta \sim L^{-2} \sim 10^{-3} \text{ }\mu\text{m}^{-2}$ – consistent with the large relaxation strength for this mechanism (eqn [28]).

Stage II is associated with the spontaneous nucleation of isolated kink pairs followed by the separation of the newly formed kinks of opposite sign. The resulting anelastic relaxation, usually associated with the Bordoni dissipation peak for deformed metals (e.g., Fantozzi et al., 1982; Seeger, 1981), is described in detail by Seeger's theory outlined in the preceding text and culminating in eqns [43]–[45]. At the still higher temperatures/larger stresses of stage III, it was envisaged by Karato that continuous nucleation and migration of kinks, possibly enhanced by unpinning of dislocations, would allow the arbitrarily large, irrecoverable strains of viscous behavior.

The relaxation times expected for geometric kink migration and kink-pair formation and migration in the Earth's upper mantle were shown by Karato (1998) to be broadly compatible with strain energy dissipation at teleseismic and lower frequencies. It was thus concluded that attenuation and associated dispersion, microcreep, and large-strain creep possibly share a common origin in dislocation glide. The results of such calculations, repeated with eqns [27], [28], and [43]–[45], are presented in Figure 14. For this purpose, we have used $a_d \sim b \sim a \sim 0.5 \text{ nm}$, $G_u = 60 \text{ GPa}$, and $\nu_{k0} \exp(S_m/k) \sim 10^{13} \text{ Hz}$ (Seeger and Wüthrich, 1976) and have chosen a relatively large value of $H_m = 200 \text{ kJ mol}^{-1}$ intended to reflect kink interaction with impurities and $\sigma_p/G = 0.01$, which, through eqn [39], fixes H_k at 162 kJ mol^{-1} (so that $2H_k + H_m$ is of order 500 kJ mol^{-1} ; cf. Karato, 1998, Figure 3). Substantially larger values of σ_p/G have been suggested (Frost and Ashby, 1982, p. 106; Karato and Spetzler, 1990, p. 407) but, when combined with Seeger's theory, yield implausibly high kink formation energies. Relaxation times have been calculated for indicative lengths of 1 and 100 μm for dislocation segments. The results of these calculations (Figure 14), like those of Karato (1998), indicate that the migration of geometric kinks could result in anelastic relaxation within the seismic-frequency band at typical upper-mantle temperatures. The much higher activation energy for the formation and migration of kink pairs (here $2H_k + H_m = 524 \text{ kJ mol}^{-1}$) results in much longer relaxation times – ranging from $\sim 10^4$ to $10^{6.5} \text{ s}$ at the highest plausible upper-mantle temperatures $\sim 1700 \text{ K}$. An effective activation energy lower by about 100 kJ mol^{-1} would be required to bring the relaxation involving kink-pair formation and migration into substantial overlap with the seismic-frequency band for typical temperatures of the convecting upper mantle as indicated by the broken line in Figure 14. Alternatively, kink-pair formation and migration might result in relaxation at the day-to-month timescales of Earth tides. Similarly, high activation energies for attenuation and creep in olivine are interpreted by Karato (1998) to imply the need for kink nucleation for both processes, whereas the low reported activation energy for attenuation in single-crystal MgO might reflect a dominant role for the migration of geometric kinks.

Emerging extrapolations of experimental forced-oscillation data for olivine to upper-mantle grain sizes and dislocation densities suggest that seismic wave attenuation might involve subequal contributions from intragranular (dislocation-related)

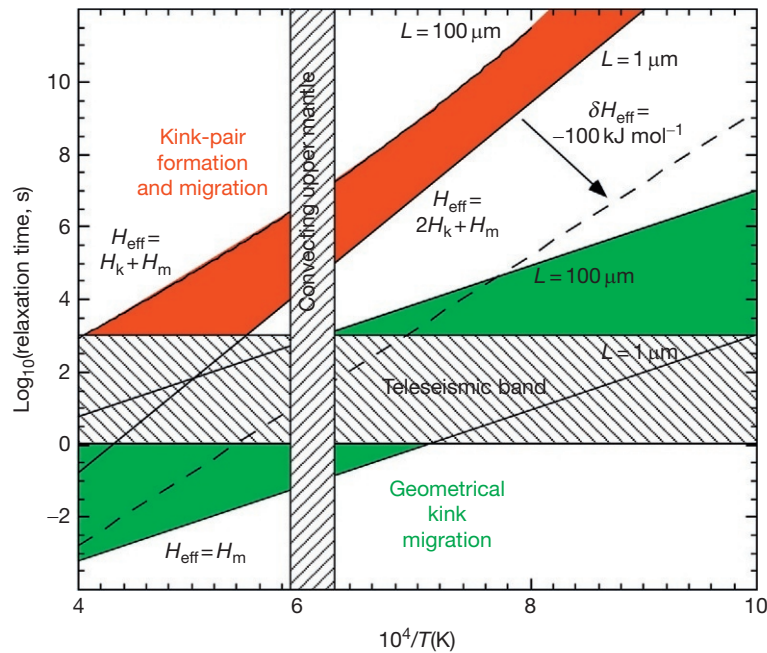


Figure 14 Computed relaxation times for Seeger's (1981) kink model of dislocation mobility. The green band represents relaxation associated with the migration of geometric kinks with segment lengths of 1–100 μm and an activation energy for kink migration $H_m = 200 \text{ kJ mol}^{-1}$. Relaxation times calculated from eqns [36]–[39] for the formation and migration of kink pairs are indicated by the red band for the same range of segment lengths and an activation energy for the formation of a single kink of 162 kJ mol^{-1} corresponding through Seeger's (1981) theory with $\sigma_p/G = 0.01$. The effect of an effective activation energy lower by 100 kJ mol^{-1} is shown by the broken line.

and intergranular (grain-boundary sliding) relaxation mechanisms (Farla et al., 2012a,b). The observation by the same authors that prior deformation in torsion is more effective than prior compressive deformation in enhancing dissipation by dislocation relaxation in torsional oscillation tests suggests that seismic wave attenuation may be anisotropic. For example, the azimuthal anisotropy of the compressional wave speed in the oceanic upper mantle and the associated polarization anisotropy whereby horizontally polarized shear waves travel faster than those with vertical polarization are both attributed to the preferred orientation of olivine resulting from activation of the dominant $[100](010)$ dislocation slip system during horizontal simple shear (Figure 15; Chapters 1.19, 2.17, and 2.20). Within this fabric, dislocations are favorably oriented for reactivation by the stress field associated with near-vertically propagating shear waves polarized parallel with the spreading direction, and accordingly, such waves should be preferentially attenuated by dislocation relaxation.

2.21.4.2 Grain-Boundary Processes

Gribb and Cooper (1998a) explained their observations of high-temperature absorption band behavior (eqn [49] with $\alpha \sim 0.35$) for a reconstituted dunite of $3 \mu\text{m}$ grain size in terms of the transient diffusional creep modeled by Raj (1975). The strong $Q^{-1} \sim d^{-1}$ grain-size sensitivity implied by this model (eqn [62]) extrapolated to millimeter–centimeter grain size seriously underestimates upper-mantle seismic wave attenuation. Gribb and Cooper (1998a) sought to resolve this discrepancy by invoking diffusively accommodated sliding on subgrain boundaries rather than on grain boundaries. It

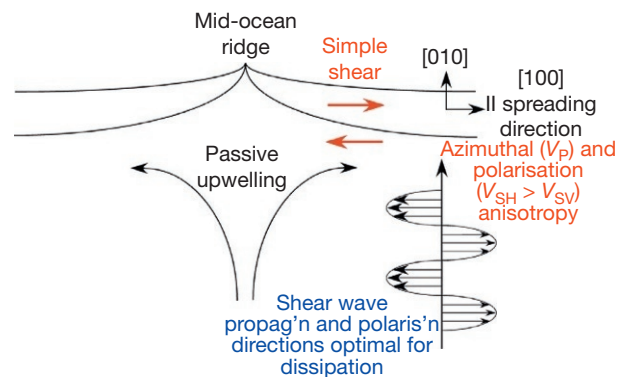


Figure 15 Anisotropy of dislocation-related seismic shear wave attenuation. Simple shear deformation in the oceanic upper mantle involves glide of the dominant $[100](010)$ dislocations that is responsible for preferred orientation of olivine grains. The observed anisotropy of seismic wave speeds is conventionally attributed to this fabric, which is also well suited to the attenuation of subvertically propagating shear waves polarized parallel with the spreading direction (Farla et al., 2012a).

was suggested that this mechanism could also reconcile the Gribb and Cooper data with those of Guéguen et al. (1989) for predeformed single-crystal forsterite. The increased attenuation resulting from prior deformation has been more naturally interpreted by others (including Guéguen et al., 1989) as *prima facie* evidence of dislocation relaxation as discussed in Section 2.21.3.1.3.

The milder grain-size sensitivity $Q^{-1} \sim d^{-1/4}$ subsequently directly measured by Jackson et al. (2002) for melt-free

polycrystalline olivine yields extrapolated levels of attenuation for mantle grain sizes more consistent with seismological observations. A generalized Burgers parameterization (eqns [4] and [78]) was used by [Faul and Jackson \(2005\)](#) to model the experimentally observed high-temperature background viscoelastic relaxation for essentially melt-free polycrystalline olivine, thereby providing an internally consistent description of the variations of both shear modulus and dissipation with frequency, temperature, and grain size. Subsequently, as explained in [Section 2.21.3](#), an additional distribution of anelastic relaxation times (eqn [79]) has been incorporated to model a subtle moderate-temperature dissipation peak and associated modulus dispersion, reflecting elastically accommodated grain-boundary sliding ([Jackson and Faul, 2010](#)). Extrapolation (principally in grain size) of this model to upper-mantle conditions establishes the baseline behavior ([Figure 16](#)) to be expected of peridotitic materials in the absence of substantial variations of dislocation density and the further complications of water and partial melting.

For example, at 100 km depth on the mantle adiabat and 1 cm grain size, shear mode dissipation is expected to exhibit a mild power-law variation (with exponent $\alpha = 0.27$) with period between $\log Q^{-1} = -1.7$ at 1 s and $\log Q^{-1} = -2.2$ at 1000 s and an Arrhenian dependence on lateral temperature variations ([Figure 16\(b\)](#)). In marked contrast, for temperatures $< 1150^\circ\text{C}$ in the much cooler thermally conductive regime of the subcontinental upper mantle, superposition of the dissipation peak of elastically accommodated grain-boundary sliding upon the background associated with diffusively accommodated grain-boundary results in a plateau of almost period- and temperature-independent dissipation in the narrow range $-2.2 < \log Q^{-1} < -2.0$ ([Figure 16\(b\)](#)). The corresponding variations of the shear modulus are displayed in [Figure 16\(a\)](#). It has thus been concluded that the lateral variations in seismic structure in the upper mantle are probably primarily of thermal origin – expressed in variations in the depth at which the conductive part of the geotherm intersects a common mantle adiabat ([Faul and Jackson, 2005](#)).

2.21.4.3 Partial Melting and the Seismic Signature of the Asthenosphere

Although solid-state viscoelastic relaxation in a dry, melt-free upper mantle can explain much of the observed variability of seismic wave speeds and attenuation, other effects, associated with partial melting (e.g., [Anderson and Sammis, 1970](#)) and/or the presence of water ([Karato and Jung, 1998](#)), may be required to explain some of the distinctive seismological characteristics of the asthenosphere. Analyses of surface wave dispersion indicate that the upper mantle beneath oceanic lithosphere is characterized by low seismic shear wave speeds at depths of 50–150 km, significant radial anisotropy with $V_{SH} > V_{SV}$, and enhanced attenuation – these effects being most pronounced and shallowest beneath young oceanic lithosphere ([Chapters 1.19, 1.25, and 2.17](#)). Furthermore, body wave studies reveal azimuthal variation of compressional wave speeds in the oceanic lithosphere, and receiver functions involving short wavelength-converted phases provide evidence for a sharp transition (< 10 – 15 km) at a depth near 70 km between (especially old) oceanic lithosphere and the lower

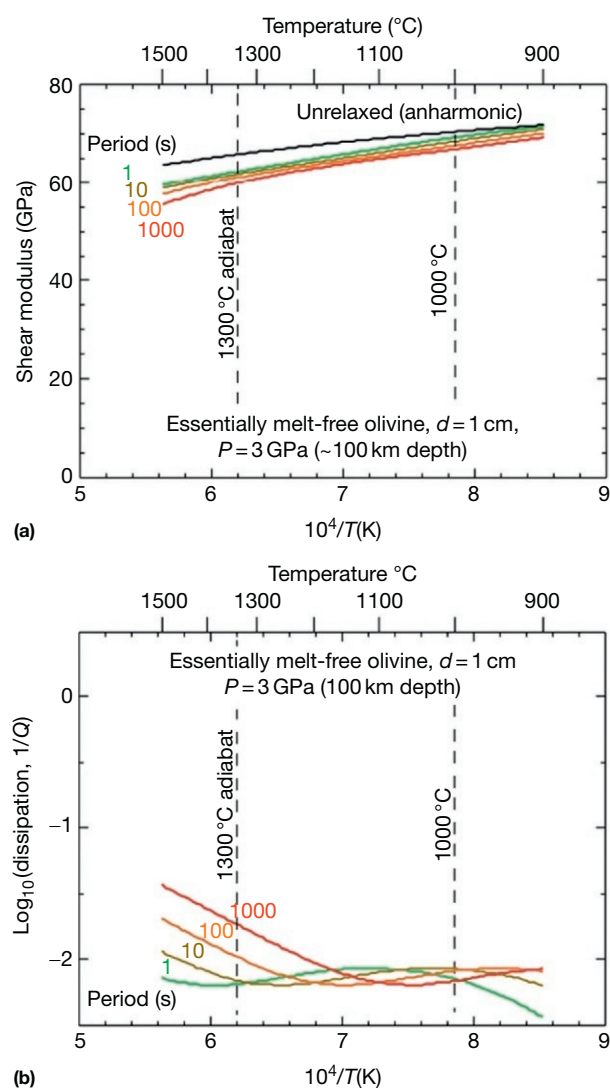


Figure 16 Extrapolation of the Burgers (background + peak) model for essentially melt-free olivine ([Jackson and Faul, 2010](#)) to conditions of grain size (1 cm), temperature, and pressure (3 GPa) representative of seismic wave propagation at a depth of 100 km in the Earth's upper mantle. Panels (a) and (b) highlight the sensitivity of shear modulus and dissipation, respectively, to variation of period at temperatures representative of the contrasting thermally conductive and convective regimes of the lithosphere and asthenosphere, respectively. Redrawn after Figure 4 of [Jackson I and Faul UH \(2010\)](#) Grainsize-sensitive viscoelastic relaxation in olivine: Towards a robust laboratory-based model for seismological application. *Physics of the Earth and Planetary Interiors* 183: 151–163.

wave speeds of the underlying asthenosphere (e.g., [Gaherty et al., 1996](#); [Kawakatsu et al., 2009](#); [Rychert and Shearer, 2009](#)).

In the presence of volatiles (water and CO_2), widespread incipient melting is expected within the asthenosphere at temperatures substantially lower than those required for major silicate melting ([Chapter 2.02](#)). Beyond the major melt-extraction zone beneath mid-ocean ridges, melt fractions $< 0.3\%$, controlled by the volatile content, are expected (e.g., [Green et al., 2010](#); [Hirschmann, 2010](#)). The influence of a

fluid, distributed in ellipsoidal inclusions of volume fraction ϕ and aspect ratio α , is a function only of the crack density parameter ε given by eqn [74]. The fractional reductions $\delta G/G$ of the shear modulus G associated with the transitions between the glued and saturated–isolated fluid-flow regimes and between the saturated–isolated and saturated–isobaric regimes are prescribed by eqns [75] and [76]. For the representative melt fraction of 0.001 (0.1%), accommodated in grain-edge tubules with effective aspect ratios no < 0.01 , wave speed reductions ($\delta V_s/V_s = (1/2)\delta G/G$) less than $\sim 1\%$ are predicted – hence the orthodox view that partial melting cannot explain the inferred large inferred reductions (5–10%) of wave speed. Kawakatsu et al. (2009) suggested that small average melt fractions may have more leverage on the speed of vertically polarized shear waves, if concentrated by stress into thin sub-horizontal layers of substantially higher melt fraction. Recently, however, Garapić et al. (2013) had confirmed previous indications (Cmíral et al., 1998) that a significant proportion of olivine grain faces are wetted by melt films of aspect ratio $< 10^{-3}$ (Section 2.21.3.3.3), raising the possibility that shear wave speeds might be much more sensitive to small melt fractions than previously thought. For example, for $\alpha = \phi = 10^{-3}$, shear wave speed reductions of 11 and 6% are predicted for the transitions between glued and saturated–isolated regimes and between saturated–isolated and saturated–isobaric regimes, respectively. Moreover, melt squirt is expected at seismic frequencies (Section 2.21.3.3.3), implying that the transition between glued and saturated–isolated regimes, with its large reduction in shear wave speed, would occur at frequencies substantially higher than those of the seismic band. Melt squirt would result in further reduction of shear wave speed and associated attenuation within the seismic-frequency band. Superposition of the squirt-related dissipation peak upon a melt-enhanced background, extrapolated to upper-mantle conditions, results in generally higher but less markedly frequency-dependent attenuation than for melt-free material under otherwise similar conditions (Faul et al., 2004, Figure 13).

2.21.4.4 The Role of Water in Seismic Wave Dispersion and Attenuation

The crystalline rocks of the Earth's upper crust are commonly pervasively cracked and often water-saturated. The sparse laboratory measurements so far performed on cracked and water-saturated low-porosity rocks are strongly suggestive of intense poroelastic relaxation (Section 2.21.3). The inference is that modulus relaxation and strain energy dissipation, associated with stress-induced fluid flow on various spatial scales, are to be expected for frequencies ranging from ultrasonic (MHz) to teleseismic (mHz–Hz). It follows that conventional (ultrasonic) measurements will tend to overestimate seismic wave speeds (especially V_p) and hence also the ratio V_p/V_s . Accordingly, high-frequency (ultrasonic) laboratory data cannot be applied directly in modeling the wave speeds and attenuation in fluid-saturated crustal rocks. Rather, it would be expected from the analysis of Sections 2.21.2 and 2.21.3 that the shear modulus of water-saturated rock at teleseismic frequencies should be comparable with that of the dry rock. Contrasting behavior is expected for the bulk modulus of the cracked rock – which

for undrained conditions will be significantly increased by water saturation (eqn [77]).

In the deeper crust and mantle, free water will typically have a more transient existence, but a small amount of water dissolved in a major nominally anhydrous mineral (like olivine or pyroxene) has the potential to significantly enhance solid-state viscoelastic relaxation, for example, by increasing the mobility of dislocations or reducing grain-boundary viscosity. There are as yet no directly relevant experimental data, but the potential has been demonstrated (Shito et al., 2006) for future analyses in which observed variations in V_p , V_s , and Q^{-1} might be combined to map variations in chemical composition, temperature, and the water content of the upper mantle.

Motivated by concerns about the capacity of partial melting to explain the sharp onset to the region of substantially reduced wave speeds at ~ 70 km depth beneath old, cold oceanic lithosphere, Karato (2012) and Olugboji et al. (2013) have revised an earlier model (Karato and Jung, 1998) that invokes a sharp contrast in water content between dry lithosphere (~ 1 wt ppm H_2O) and damp (100 wt ppm H_2O) asthenosphere. From eqn [60] of Section 2.21.2.3.2.5, Karato and his colleagues predicted that the relaxation time τ_c should decrease by two to four orders of magnitude between the dry oceanic lithosphere and the underlying damp asthenosphere. Under these circumstances, conditions in the lithosphere would be unrelaxed with respect to elastically accommodated grain-boundary sliding, with a sharp transition to the lower wave speeds of relaxed conditions associated with the proposed discontinuity in water content.

2.21.4.5 Bulk Attenuation in the Earth's Mantle

If pressure-induced changes in the proportions of coexisting crystalline phases were to result in relaxation of the bulk modulus within the seismic-frequency band (for which there is little seismological evidence), conditions would be most favorable in the upper mantle and transition zone. It is here that relatively high temperatures facilitating rapid phase transformation are combined with phase transformations involving substantial density contrast. Consider, for example, the olivine–wadsleyite transformation with an *in situ* density contrast of $\sim 6\%$. This is diluted in the pyrolite composition by an almost equal volume of the $(M,Al)(Si,Al)O_3$ ($M = Mg, Fe$) component playing an essentially passive role. However, the presence of the latter component and partitioning between it and the M_2SiO_4 phases reduces the width of the binary loop to $\delta P < 0.3$ GPa (Irifune and Isshiki, 1998; Stixrude, 1997; Weidner and Wang, 2000). Thus, eqn [66] for the relaxation strength yields $\Delta_v \sim (150 \text{ GPa}/0.3 \text{ GPa})(0.03) = 15$, but of course, any resulting compressional wave attenuation would be confined to a layer of thickness ~ 10 km comparable with the seismic wavelength. For the wider two-phase loop of the pyroxene–garnet phase transformation, $\Delta_v \sim (150 \text{ GPa}/5 \text{ GPa})(0.03) = 0.9$, so that any seismic wave attenuation, although of lower intensity, would more readily be observed. The large relaxation strengths for this process mean that it probably plays an important role somewhere in the Earth's wide mechanical relaxation spectrum. Relaxation times comparable with seismic periods have been estimated (Li and Weidner, 2008; Ricard et al., 2009). However, the absence of seismological evidence

of strong bulk dissipation in the transition zone (Chapter 1.25) suggests that such relaxation may actually occur at substantially longer periods.

Significant bulk dissipation Q_K^{-1} may arise at the shorter periods of teleseismic waves, from the elastic heterogeneity of aggregates of anisotropic mineral grains as explained in Section 2.21.3. Values of $Q_K^{-1}/Q_G^{-1} \sim 0.01$ were calculated for polycrystalline forsterite and a peridotitic composite, representative of upper-mantle materials by Budiansky and O'Connell (1980). For the mixture of silicate perovskite and magnesio-wüstite that dominates the mineralogical makeup of the Earth's lower mantle, the relaxation of the bulk modulus is expected to decrease with increasing pressure along the high-temperature adiabat from $\sim 2\%$ at zero pressure to $<1\%$ in the deepest mantle (Heinz et al., 1982; Jackson, 1998). Thermo-elastic relaxation (eqn [54]) may enhance the bulk dissipation that is the direct consequence of elastic heterogeneity, to levels sufficient to explain the modest amount of bulk dissipation evident in the damping of the low-order radial modes of free oscillation of the Earth (Budiansky et al., 1983).

As discussed in Section 2.21.2.4.1, partial relaxation of the bulk modulus and associated strain energy dissipation may arise from small changes in melt fraction and hence density in response to the fluctuating mean stress associated with a compressional wave (Li and Weidner, 2013). However, the intensity of such effects may be mitigated by the low melt productivity (pressure sensitivity of melt fraction) to be expected in the regime of incipient melting (e.g., Hirschmann, 2010).

2.21.4.6 Migration of Transformational Twin Boundaries as a Relaxation Mechanism in the Lower Mantle

It has been suggested by Harrison and Redfern (2002) that the mobile transformational twin boundaries that are clearly responsible for intense dissipation and associated modulus relaxation observed in the laboratory in some pervasively twinned perovskite crystals might also operate in the Earth's silicate perovskite-dominated lower mantle. Pinning of such domain walls by oxygen vacancies as in LaAlO_3 perovskite would result in anelastic relaxation times for lower-mantle conditions much shorter than teleseismic periods. Stronger pinning of domain walls by defects, impurities, and grain boundaries would be required for relaxation times within the seismic band (Harrison and Redfern, 2002). Indeed, pinning so effective as to eliminate significant anelastic relaxation has subsequently been observed in orthorhombic $(\text{Ca,Sr})\text{TiO}_3$ perovskites (Daraktchiev et al., 2006). More critically, however, substantially different microstructures are to be expected in the silicate perovskites of the lower mantle. The sustained operation of tectonic stress over geologic timescales should enlarge the domains of any transformational twins that are favorably oriented with respect to the ambient stress field resulting in a population of mainly single-domain grains and incidentally some degree of lattice-preferred orientation. Twin boundary migration can therefore play a major role in seismic wave attenuation in the lower mantle only if twinning contributes significantly to the prevailing tectonic deformation (Carpenter and Zhang, 2011).

2.21.4.7 Solid-State Viscoelastic Relaxation in the Earth's Inner Core

The combination of low (but finite) rigidity and marked attenuation that characterize the Earth's inner core has long been regarded as highly anomalous and has often been explained in terms of partial melting, as reviewed by Jackson et al. (2000) (see also Vočadlo, 2007, Chapter 2.06). However, the relatively low value of G/K and hence high Poisson's ratio ($\nu = 0.44$) are at least in part the expected consequence of the compression of a close-packed crystalline solid (Falzone and Stacey, 1980). First-principles calculations suggest values of ν of 0.29–0.32 at inner core densities and 0 K (Vočadlo et al., 2003a, Table 1) and the possibility of a further substantial increase due to the usual anharmonic influence of temperature (Steinle-Neumann et al., 2003; Vočadlo, 2007). Laboratory measurements reviewed in the preceding text have revealed pronounced viscoelastic relaxation in both b.c.c. and f.c.c. phases of mildly impure iron at homologous temperatures (T/T_m) reaching 0.6 and 0.9, respectively (Jackson et al., 2000). Given the high homologous temperature ($T/T_m \sim 1$) of the inner core, intense solid-state viscoelastic relaxation is inevitable. The experimental evidence for solid-state viscoelastic relaxation in iron would have direct relevance to the Earth's inner core if the b.c.c. phase were to be stabilized by high temperature and/or the accommodation of light alloying elements (Vočadlo, 2007; Vočadlo et al., 2003b). The inevitable contribution of solid-state relaxation to the observed seismic wave attenuation ($Q_G^{-1} \sim 0.01$ – 0.02) and to any required viscoelastic relaxation of the shear modulus ($\sim 1.5\%$ per decade of frequency for $Q^{-1} = 0.01$) must therefore be considered before partial melting is invoked (e.g., Vočadlo, 2007).

2.21.5 Summary and Outlook

This survey of viscoelastic relaxation mechanisms potentially relevant to the Earth's deep interior highlights the prospects for convergence between theory and experimental observations. Long-established theoretical models provide plausible, if highly idealized, descriptions of viscoelastic relaxation associated with dislocation motion and grain-boundary sliding. The stress-induced redistribution of an intergranular fluid is similarly well described theoretically. That this substantial framework has not yet been more thoroughly tested against experimental observations is attributable in part to limitations in the experimental methods that have been overcome only relatively recently. The pioneering experimental work of the 1950s and 1960s focused on low-temperature internal friction peaks in metals investigated with resonant (i.e., pendulum) techniques. This isochronal approach has the major disadvantage that it provides no opportunity to observe the relaxation spectrum by continuous variation of frequency under isothermal conditions. More recently, there has been growing recognition of the superiority of mechanical spectroscopy methods in which subresonant forced oscillations probe the relaxation spectrum under isothermal high-temperature conditions affording the benefit of a stable microstructure (Berckhemer et al., 1982; Gadaud et al., 1990; Getting et al., 1997; Gribb and Cooper, 1998b; Jackson and Paterson, 1993; Schaller et al., 2001; Takei et al., 2011; Woignard et al., 1981). This technique

is particularly well suited to investigation of the high-temperature background – the monotonic variation of Q^{-1} with frequency and temperature that typically dominates the dissipation at high temperature and low frequency. In addition, complementary microcreep tests are now being more widely used to distinguish between recoverable (anelastic) and permanent (viscous) strains.

Sustained application of these improved methods to well-characterized specimens of geologic and ceramic materials is beginning to elucidate the microscopic processes responsible for their high-temperature viscoelastic relaxation. The consistent picture emerging from studies of fine-grained polycrystalline materials lacking a dispersed secondary phase of low viscosity is dominated by a broad absorption band (eqn [49]) involving mild frequency dependence of Q^{-1} and an Arrhenian variation with temperature with an activation energy often comparable with that for creep. However, thorough probing of the low-loss transition between elastic and anelastic behaviors is providing tantalizing evidence of a subtle dissipation peak with $Q^{-1} \sim 10^{-2}$ attributable to elastically accommodated grain-boundary sliding.

Although so far only rarely determined, the grain-size sensitivity of viscoelastic relaxation is potentially diagnostic of the relative contributions of grain-boundary and intragranular mechanisms. For example, the mild grain-size sensitivity of the dissipation and dispersion measured on fine-grained polycrystalline olivine suggests that such grain-boundary processes contribute significantly – but admits the possibility also of significant intragranular contributions.

Dislocation damping is a likely intragranular contributor to seismic wave attenuation especially in the shallower parts of the upper mantle where seismic anisotropy attests to the development of olivine lattice-preferred orientation by dislocation creep. The potential of stress-induced migration of (pre-existing) geometric kinks (Karato, 1998; Figure 14) to cause significant relaxation within the seismic-frequency band has been demonstrated. Building upon the pioneering study of Guéguen et al. (1989) of dislocation damping in upper-mantle materials, Farla et al. (2012a,b) have recently demonstrated a correlation between dissipation and dislocation density. Further systematic studies of untreated and variously predeformed specimens, including olivine single crystals, will be needed to more clearly separate inter- and intragranular relaxation processes and to clarify the nature of dislocation relaxation including the role of pinning and the relative contributions of subgrain and subgrain-boundary dislocations. The possibility that both grain-boundary and dislocation relaxation are enhanced by the presence of small concentrations of water-related defects under water-undersaturated conditions relevant to the Earth's mantle remains to be explored experimentally.

Both dislocation-related and grain-boundary relaxation processes thus have the potential to make substantial contributions to seismic wave dispersion and attenuation. Dislocation relaxation should become progressively more important with increasing grain size for two reasons: (1) prior/ongoing tectonic deformation by dislocation rather than diffusional creep is required to generate an appropriate density of mobile dislocations, and (2) low grain-boundary area per unit volume will diminish the relative importance of grain-boundary relaxation. Thermal activation of the mobility of the defects

responsible for the dominant high-temperature background means that solid-state viscoelastic relaxation will become progressively more intense as the relevant solidus is approached. Solid-state relaxation mechanisms may thus account for most of the seismologically observed variation of wave speeds and attenuation.

However, relaxation mechanisms associated with partial melting and phase transformations must also contribute at least locally to viscoelastic relaxation in the mantle. Recent experimental observations suggest that the small melt fraction (generally <0.3%) arising from incipient melting in the asthenosphere may wet a significant proportion of olivine grain boundaries. Such thin melt films would be much more effective than grain-edge tubules in reducing the shear wave speed. Moreover, a timescale within the seismic band is predicted for melt squirt between adjacent grain-boundary films. Experimental observations of a melt-related dissipation peak, superimposed upon the dissipation background, and associated shear modulus dispersion have accordingly been reinterpreted in terms of melt squirt. The implications for the asthenosphere are reduced wave speeds and nearly frequency-independent attenuation across wide ranges of conditions (Faul et al., 2004). Stress-induced changes in the melt fraction of the incipiently molten asthenosphere may result in partial relaxation of the bulk modulus, but such effects might prove to be seismologically unobservable. In parts of the transition zone, stress-induced variations of the proportions of coexisting phases may result in relaxation of the bulk modulus and associated dissipation of strain energy, probably at periods substantially longer than those of seismic waves.

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2.22 Properties of Rocks and Minerals, High-Pressure Melting

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2.22.1 Melting Properties of Lower Mantle Components

The lower mantle encompasses the pressure range from 24 to 135 GPa at the core–mantle boundary (CMB). The three major components are (Mg,Fe)SiO₃-perovskite (PV) and (Mg,Fe)O-magnesiowüstite (MW), making up about 90%, and CaSiO₃-PV. With regard to melting, the PV phase drew most of the attention in early theoretical and experimental work. Based on the phase diagram measured in multianvil presses at lower pressures (to about 25 GPa) and the very high-melting temperature of MgO at ambient pressure, it was believed that the eutectic composition of the lower mantle lies near the composition of the major component (Mg,Fe)SiO₃-PV, and therefore, the eutectic melting temperature of the lower mantle would be close to that of the end-member PV. However, later measurements made in the laser-heated diamond-anvil cell (DAC) have shown that this assumption was incorrect. These measurements indicate that at about 60 GPa and 4200 K, the two melting curves of PV and MW cross and PV becomes the lower temperature melting phase. Thus, with increasing depth, the eutectic melting composition would have to move away from that of PV and the first partial melt would be rich in MW. The strong temperature rise in the thermal boundary layer at the bottom of the lower mantle combined with iron partitioning into MW could cause gravitational segregation of this liquid MW-rich phase, which could explain the unusual seismic signature observed near the CMB (Boehler, 2000).

2.22.2 Melting of (Mg,Fe)SiO₃-PV

Both the early theoretical and experimental estimates of the melting temperature of PV for lower mantle pressures showed extremely large differences. The first molecular dynamics (MD) calculations were 2000 K above the first DAC results even at pressures as low as 30 GPa and these early DAC measurements showed positive and negative slopes and even a combination of both (see references in Zerr and Boehler, 1993). The extremely large variations clearly demonstrated the experimental and

computational difficulties to determine the melting of minerals at high compression. However, the development of CO₂ laser heating allowed heating of minerals directly without metal absorbers in inert gas pressure media, such as argon, providing more accurate melting measurements of single-crystal minerals and even multicomponent systems at mantle pressures (Zerr and Boehler, 1993, 1994; Zerr et al., 1997, 1998). It is now well accepted that the melting temperatures of PV drastically increase with increasing pressures as evident from Figure 1. The melting temperatures of Zerr and Boehler (ZB) and Shen and Lazor agree well within the experimental uncertainty, which is typically ± 200 K. Similar high melting slopes were measured for Ca-PV (Shen and Lazor, 1995; Zerr et al., 1997).

The melting of the MgSiO₃–Mg₂SiO₄ system has been measured by shock compression (for a summary, see Ahrens et al. (2009) and Chapter 2.16). The estimated shock temperatures remain uncertain, and there is the additional complication that the solid shock conditions for silicates overdrive the melting curve, resulting in an uncertainty of at least ± 500 K. However, the estimated melting temperature for MgSiO₃ at the CMB pressure of 135 GPa of 5300 K is in reasonable agreement with ab initio calculations (Stixrude, 2005) and two-phase quantum MD simulations (Belonoshko et al., 2005). Combining the DAC melting curve of ZB with shock measurements on MgSiO₃ glass (Akins et al., 2004; Luo et al., 2004) suggests a significant flattening in the melting curve above 62 GPa, the highest pressure attained experimentally, and the best estimate for the melting temperature of PV at the CMB is between 5500 and 6000 K.

Sweeney and Heinz (1998) using conventional YAG laser-heating techniques without an argon pressure medium made measurements of about 80 GPa. At lower pressures, the melting temperatures agree with ZB within their experimental uncertainties, but their melting slope above about 40 GPa is almost zero, which is in disagreement with the other estimates. There are, to date, no additional DAC data on PV melting in the pressure range relevant to the Earth.

Spaulding et al. (2012) had reported laser-driven shock experiments, made employing the LLNL and Rochester lasers to examine the high temperature–pressure phases of MgSiO₃. With

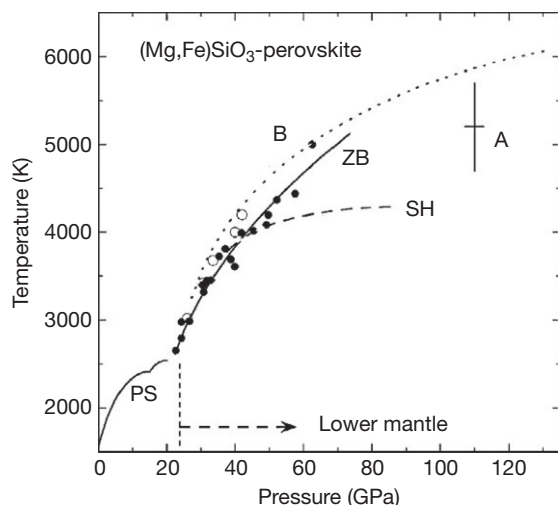


Figure 1 Melting temperatures of Mg–Si-perovskite from different studies – diamond-anvil cell measurements: black dots, Zerr and Boehler (1993) (ZB); open circles, Shen and Lazor (1995); dashed curve, Sweeney and Heinz (1998) (SH); calculations: dotted curve, Belonoshko et al. (2005); shock melting point (A), cross by Akins et al. (2004) and Luo et al. (2004). PS is the solidus of upper mantle peridotite. There is a consensus that the melting temperatures of PV rise very steeply, but the amount of flattening at higher pressures is still not clear.

increasing pressure, the low-temperature melt transforms to a high-density metallic liquid phase with an increase in density of 10% between 300 and 400 GPa, over a wide range of temperature, suggesting complex liquid formation in magmas at multi-Mbar pressures. Their experimental measurements extend the Hugoniot equation of the state of MgSiO_3 to 950 GPa.

2.22.3 Melting of MgO

At ambient conditions, MgO has the NaCl rock-salt (B1) structure, which is known from experiments to be stable to 227 GPa (Duffy et al., 1995). Calculations now predict the B1 phase transforms to B2 at about 490 GPa (Belonoshko et al., 2010). The room temperature isotherm and the elasticity have been measured in DACs to 55 GPa (Zha et al., 2000). Due to the high initial melting temperature of MgO (3060 K at 1 bar), the only direct experimental determination of the melting curve has been that using a laser-heated DAC to 32 GPa and 4000 ± 300 K (Zerr and Boehler, 1994). The melting curve is rather flat and resembles those of ionic solids at high compression (Boehler et al., 1996, 1997). Since these experiments cover only the first 25% of the mantle pressure range, their melting slope ($dT/dP = 36 \text{ K GPa}^{-1}$) plays an important role in constraining theoretical predictions (Aguado and Madden, 2005; Alfe, 2005; Belonoshko and Dubrovinsky, 1996; Strachan et al., 1999; Vocadlo and Price, 1996). More recently, multianvil experiments were carried out on iron-rich solid solutions of FeO and MgO in a multianvil press to 7 GPa. Estimates of the pressure dependence of melting of the MgO end-member require long extrapolations but resulted in a very steep melting curve (Zhang and Fei, 2008). These estimates are in stark disagreement with the DAC experiments. However, it is important to note that the DAC measurements on PV and MgO used identical techniques to determine melting and measure temperatures.

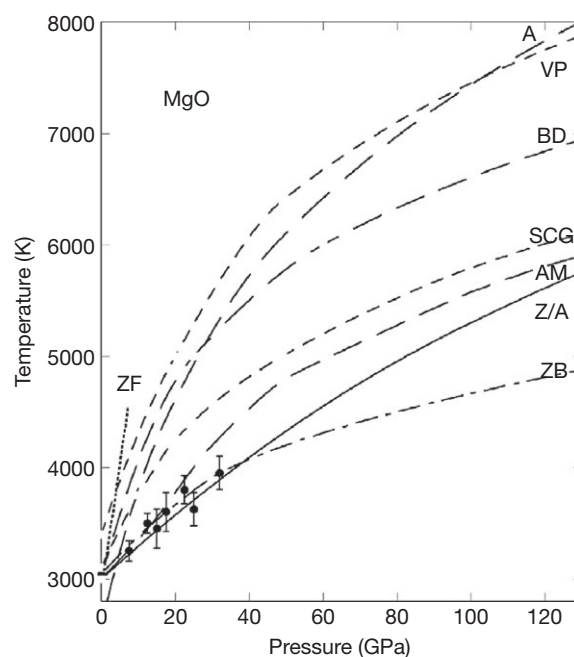


Figure 2 MgO melting: experiment and theory. The only direct measurements are from ZB to 32 GPa (Zerr and Boehler, 1994). ZF (Zhang and Fei, 2008) is derived from a multianvil study on iron-rich FeO–MgO compositions. Theory: AM (Aguado and Madden, 2005) and their new extrapolation Z/A of the ZB data; SCG (Strachan et al., 1999); BD (Belonoshko and Dubrovinsky, 1996); VP (Vocadlo and Price, 1996); A (Alfe, 2005); for description, see text.

Figure 2 shows a comparison of the experimental and predicted theoretical melting curves. An extrapolation of the ZB measurements leads to an estimated melting temperature of about 5000 K at the CMB using a Lindemann equation with a Grüneisen parameter of 1.3, determined from this measured curve (Zerr and Boehler, 1994). The measured melting temperatures are substantially lower than all the theoretical results, which among themselves are in poor agreement and exhibit a widespread.

Despite their apparent simplicity, theoretical calculations for the oxides are complicated by the fact that the oxygen anion, O^{2-} , which does not exist in the free state, is stabilized by its local environment in the solid phase (Watson, 1958). This complicates any accurate modeling of the liquid phase. Oxygen anions in oxide materials have been characterized as having diffuse electronic charge distributions and large polarizabilities that make quantitative modeling difficult (Vidal-Valet et al., 1978). In MgO, the charge densities are close to the situation Mg^+O^- . For the other alkaline oxides, the charge densities imply $\text{X}^{2+}\text{O}^{2-}$. It was shown (Lacks and Gordon, 1993) that the O^{2-} anion can be distorted in the direction of neighboring cations creating a nonspherical charge distribution that lowers the Coulomb energy. Since the liquid is not locked into a periodic structure, it can be influenced to lower its energy by forming local arrangements differing from the usual hard-sphere-like spherically symmetrical local structures employed in liquid simulations. This property may be at least in part responsible for the surprisingly large range of the theoretical predictions plotted in Figure 2.

In order to include the presence of possible local structures in their simulations, Strachan et al. (1999) (SCG) and Aguado and Madden (2005) (AM) employed a priori methods to obtain transferable potentials. Transferable potentials provide an empirically derived description of interatomic forces over a range of perfect and defective crystal structures, liquid phases, and low coordinated sites as those encountered at surfaces and clusters. Transferable potential parameters may be obtained by fitting to interatomic forces and stress tensor components that are obtained by ab initio methods for a large number of atomic configurations. Transferability is essential in the case of melting because in contrast to the solid, the liquid is not restricted to a symmetrical periodic structure.

To calculate melting, SCG used the 'transferable' potential for both the solid and liquid phases to calculate the enthalpy and volume changes. The melting curve was obtained by integrating the Clausius–Clapeyron equation. They also predicted a B1–B2 transition at 400 GPa and 0 K and a melting temperature of ~6100 K at the CMB. AM also developed a transferable potential, which they also used to calculate the volume and enthalpy and locate the melting curve by integrating the Clausius–Clapeyron equation. They found that at 1 bar, MgO melts from a wurtzite structure with a melting slope in good agreement with the slope determined by ZB. Near 10 GPa, the wurtzite structure reconverts to rock salt and lies in agreement with the ZB melting curve to the highest measured pressure of 32 GPa. AM predicted the temperature of ~5950 K at the CMB.

Based on an inspection of the DAC data, AM noted that the extrapolation procedure of ZB, to predict a melting temperature of ~5150 K at the CMB, has a large uncertainty. Since their calculations are in reasonable agreement with ZB up to about 23 GPa, AM combined their calculations with the experimental data and constructed a revised melting curve. The new melting curve predicts a temperature of 5850 K at the CMB, higher than ZB by 700 K, but lower than other theoretical estimates.

Intermolecular potentials fitted to the room temperature solid properties have been used to calculate the melting curve by the method of coexisting phases (Belonoshko and Dubrovinsky, 1996 (BD); Vocadlo and Price, 1996). By employing a potential determined empirically from fits to solid-state data, for both the solid and liquid, they assumed implicitly that the potential is transferable from solid to liquid, which is questionable in the case of MgO. In the most recent study, Alfé (2005) calculated an MgO melting curve by carrying out simulations of the coexisting phases, but rather than employing effective interaction potentials, he used first-principles density functional theory (DFT). His temperatures are the highest of those calculations reported. The coexisting phase method employed by BD and Alfé is an approximation that amounts to determining a state of mechanical equilibrium between the two phases, $(P, T)_s = (P, T)_l$, but not to thermodynamic equilibrium, $(P, T, G)_s = (P, T, G)_l$. The problem is that the formation of local structures in the liquid may lower the internal energy, hence the Gibbs energy, without significantly altering the pressure. While the coexisting phase method can be useful in many situations, the method is not rigorous.

The lowest calculated melting slopes, in best agreement with experiment, are those by SCG and AM, who employed transferable potentials for both phases and employed the rigorous Clausius–Clapeyron equation to calculate the melting

curve. Since the number of configurations employed in developing their potentials was necessarily finite, their reported melting pressures should be considered as an upper bound. Consequently, we believe that a best estimate of the melting temperature of MgO at the CMB is in the range 5150–5850 K. Shock experiments for single crystal of preheated MgO were carried out over the pressure range 102–203 GPa, and temperature measurements were made via optical pyrometry (Fat'yanov et al., 2009, 2011). Final temperatures ranged from roughly 3800 to 6500 K, and no evidence was found for melting or any phase transitions were detected. Laser-driven shock-wave experiments to 1.4 terapascal (TPa) reveal a sequence of two-phase transformations: from B1 (sodium chloride) to B2 (cesium chloride) crystal structures above 0.36 TPa and from electrically insulating solid to metallic liquid above 0.60 TPa (McWilliams et al., 2012).

In summary, the only static (DAC) melting measurements for MgO (Zerr and Boehler, 1994), made to 32 GPa, and now almost 20 years old, reveal a relatively flat melting curve. Theoretical predictions vary significantly among themselves and show a steeper melting. McWilliams et al. (2012), employing laser-driven shock experiments, reported having observed melting of MgO near 400 GPa (10 000 K). While their results extrapolate nearly linearly from the DAC measurements, overall, the melting behavior of MgO remains inconclusive.

2.22.4 Partial Melting in the Lower Mantle

The lower mantle likely behaves as a eutectic system with the end-members MW and PV. Even though the study of the melt properties of these end-members is of fundamental importance, their melting temperatures may have little direct relevance to mantle melting. However, both static DAC measurements and shock experiments can be used to put constraints on the solidus of the lower mantle. DAC melting measurements for a material composed of all the major elements in the lower mantle – O, Si, Mg, Fe, Al, Ca, Ti, Cr, Ni, and Na (the sample was a glass with a pyrolite composition) (Zerr et al., 1998) – showed a significant lowering of the melting temperature with respect to PV and MW (LM rock in Figure 3). The solidus temperatures in these experiments were bracketed on the basis of textural changes observed in the recovered samples from a series of P – T runs. The measured pyrolite solidus for this multicomponent system lies approximately parallel to the melting curve of MgO but is offset to lower temperatures by about 1000 K. These observations are in agreement with the shock melting temperature of Mg_2SiO_4 olivine at 130 GPa and 4300 K (Holland and Ahrens, 1997). The olivine composition ($\text{MgO}:\text{MgSiO}_3 = 1:1$) may well represent the eutectic composition in the MgO–PV system (see Figure 4). From these measurements, we conclude that a reasonable estimate for the solidus temperatures at the CMB (135 GPa) is about 4300 K, definitely much lower than any prediction for the end-members MgO and PV. The predicted simplified phase diagram for the lower mantle is shown in Figure 4. Thus, partial melting is likely to occur in the lowermost mantle, taking the experimental evidence from both static and dynamic studies and the predicted core temperature at the CMB (Boehler, 2000).

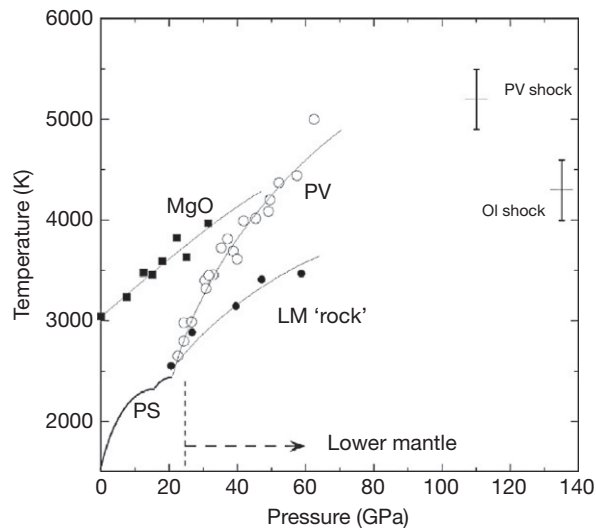


Figure 3 Melting temperatures of lower mantle components measured in the diamond-anvil cell by Zerr and Boehler (1993, 1994) and Zerr et al. (1998). PS is the solidus of upper mantle peridotite. The melting curves of MgO and PV are likely to cross at about 60 GPa and their melting temperatures in the deep mantle may be similar if the PV melting continues to flatten (see text). The eutectic temperatures of a pyrolite system (LM rock) are about 1000 K below that of the end-members MgO and PV. Shock melting points for MgSiO_3 -PV (Akins et al., 2004) and Mg_2SiO_4 ($\text{MgO}:\text{MgSiO}_3 = 1:1$) (Holland and Ahrens, 1997) are also shown.

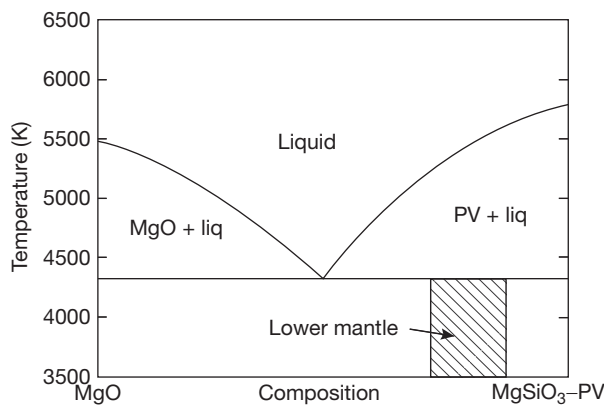


Figure 4 Schematic eutectic phase diagram of MgO and PV with predicted melting temperatures at the CMB (see text): The eutectic temperature is about 1000 K lower than that of the end-members PV and MgO. For comparison, the shock temperature of olivine ($\text{MgSiO}_3:\text{MgO} = 1:1$) at 130 GPa is 4300 ± 300 K (Holland and Ahrens, 1997) and that of MgSiO_3 is 5200 ± 500 K at 110 GPa. The composition of the lower mantle is accepted to be closer to PV than to MgO, and therefore, a partial melt must be MgO-rich (Boehler, 2000).

It should be pointed out that the DAC experiments on the pyrolite glass and those on PV, MgO, and MW were made using identical experimental setups, temperature measurements, and melt detection, and they were carried out by the same persons. These measurements resulted in an interesting observation that may be relevant to the chemical composition of a partial melt: The melting slopes between PV and MgO are entirely different

and the two melting curves are likely to cross each other between 50 and 60 GPa (see Figure 3). From this fact, one must conclude that the melting temperature and chemical composition of a partial melt in the mantle will change with depth. The important task for future work will be the investigation of the nature and chemical composition of this melt. This melt is likely enriched in MgO (MW) because the lower mantle composition is closer to PV than to MgO, as shown schematically in Figure 4. Additionally, iron partitioning into this MW-rich liquid phase may cause gravitational segregation, thus explaining the unusual signature of the seismic signal near the CMB.

2.22.4.1 Iron Phase Diagram

One of the major constraints on the Earth's thermal gradient and dynamics and the temperature at the center of the Earth is the melting temperature of iron at the pressure conditions of the inner core boundary (ICB) (330 GPa, or 3.3 Mbar). The two techniques capable of generating very high pressure and temperature conditions, shock compression and laser heating in DACs, have associated weaknesses. Despite the fact that in combination the experiments cover a large portion of the pressure and temperature range up to the ICB, a full understanding of the phase diagram, elasticity, structure, and viscosity of both solid and liquid is lacking. The primary drawback to shock compression experiments is their short timescale and that for most cases only one melting point can be obtained where the Hugoniot crosses the melting curve. In many cases, this crossing point is difficult to locate precisely. For most materials, shock velocity measurements are required to detect melting. Moreover, the shock temperatures have to be calculated using a thermal model. However, an often overlooked feature of shock experiments is that the measured parameters, shock velocity (us), and particle velocity (up) can provide useful insight into the nature of the shocked phases.

For the DAC, the weakness is the small sample size making melt detection difficult and causing high-temperature gradients. The relatively long heating durations may cause chemical reactions between the sample and the pressure medium.

Given the complexities and the drastic difference in these experimental approaches, the agreement between static and shock experiments for many materials is remarkable. Unfortunately for iron, however, the data using shock compression and laser-heated DAC (LHDAC) experiments and from theory show an apparent disagreement ranging from 4800 to 7600 K for the ICB. This appears to be the consequence of an incomplete understanding of the high-temperature phase diagram.

2.22.4.2 Stability Field of hcp Iron

At ambient conditions, iron has a bcc structure and transforms into hcp at 13 GPa (Boehler et al., 1990). x-Ray diffraction (XRD) measurements at room temperature found the hcp phase stable up to about 300 GPa (Mao et al., 1990) and more recently even over a very large P - T range of 377 GPa and 5700 K (Tateno et al., 2010). The fcc-hcp phase boundary has been measured in the DAC and in a multianvil press to 40 GPa and 1600 K (Boehler, 1986; Kubo et al., 2003; Mao et al., 1987) and extended to the melting curve (Boehler,

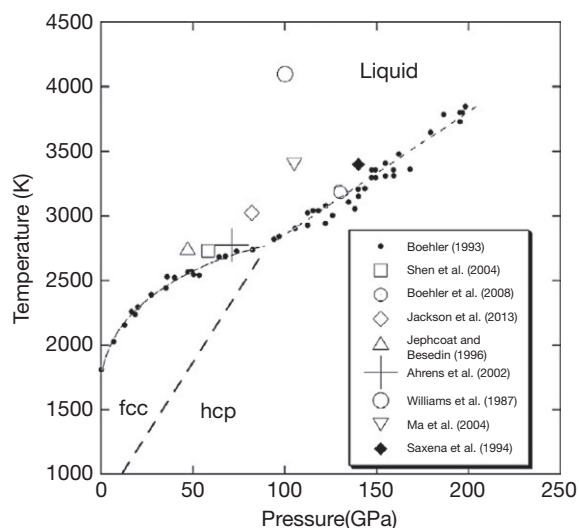


Figure 5 Iron phase diagram. Melting: solid dots are older measurements (Boehler, 1993). For simplicity, only the highest P - T data points of melting for other measurements are shown (Boehler et al., 2008; Jackson et al., 2013; Jephcoat and Besedin, 1996; Ma et al., 2004; Saxena et al., 1994; Shen et al., 2004; Williams et al., 1987). Shen's measurement (Shen et al., 2004) is the last solid point measured by x-ray diffraction. The cross is a shock melting measurement on preheated iron (Ahrens et al., 2002). The fcc-hcp phase boundary is an average of Mao et al. (1987), Kubo et al. (2003), and Boehler (1993). Dashed lines are guides to the eye.

1993). These data are in good agreement. In combination with shock melting, new x-ray measurements point to an fcc-hcp-liquid triple point near 80 GPa (see Figure 5).

2.22.4.3 DAC Melting Measurements

Numerous experimental measurements for Fe melting have been made using LHDACs (Boehler, 1993; Boehler et al., 2008; Jackson et al., 2013; Jephcoat and Besedin, 1996; Ma et al., 2004; Saxena et al., 1994; Shen et al., 2004; Williams et al., 1987) as shown in Figure 5. Also shown in the figure are shock velocity measurements on preheated iron at 71 GPa and 2775 K (Ahrens et al., 2002). The maximum pressure for which iron melting temperatures have been reported from LHDAC experiments is 200 GPa at temperatures of 4000 K (Boehler, 1993). These measurements, using mainly simple visual methods to detect melting, are shown by the black dots in Figure 5. For simplicity, only the highest P - T melting points are shown for the other measurements. Below 100 GPa, the more recent measurements show agreement within the experimental uncertainty. The causes for the shown discrepancies at higher pressures can be understood in view of earlier laser instabilities and very high temperature gradients and of the different methods with which temperatures were measured and melting was detected. Moreover, chemical reactions associated with the use of different pressure media cannot be ruled out in some experiments. A detailed analysis of these discrepancies is difficult, because often the experimental procedures were not adequately described.

In recent years, the previous problems associated with large temperature gradients could be significantly reduced due to the development of more powerful and more stable lasers. Larger hot spots on the sample reduce problems in the temperature measurement. Done properly, temperature measurement using the Planck emission spectroscopy is robust and the uncertainties are of the order ± 200 K, at the highest temperatures considering extreme variation in the emissivities in the wavelength range used in these measurements.

The detection of melting is more challenging, but there are a number of physical property changes between solid and liquid that are measurable in the DAC. For iron, discontinuous changes in the resistivity of thin wires (Boehler, 1986) and changes in reflectivity and laser power (Boehler, 1993; Boehler et al., 1990; Saxena et al., 1993) have been measured. The most drastic change between solid and liquid is the loss of strength at melting. This often causes motion on the sample surface that can be made visible with the speckle pattern of an argon-laser beam (Boehler et al., 1996; Jephcoat and Besedin, 1996). These methods were compared in some experiments with the first observation of microscopic melt features on the surface of the quenched sample for iron (Boehler, 1993) and for a number of other metals (Errandonea et al., 2001; Yang et al., 2012).

Probably, the most conclusive melting criterion is by XRD. Diffusive x-ray scattering from laser-heated iron samples has been documented above the melting temperature by Shen et al. and by Boehler et al. to 58 and 130 GPa, respectively (Boehler et al., 2008; Shen et al., 2004), as shown in Figure 5. More recent x-ray measurements use synchrotron Mössbauer spectroscopy to detect melting up to 82 GPa (Jackson et al., 2013), and melting of iron has been observed in x-ray absorption spectra to 78 GPa (Boehler et al., 2009). Both of these methods have the advantage over diffraction in that the spectra do not depend on the crystallinity of the sample, which changes significantly during heating cycles. It should be pointed out that in order to measure melting using x-ray methods, a finite amount of material has to be in the molten state and melting temperatures may therefore be overestimated due to temperature gradients within the sample. In summary, there exists rather good agreement between the visually measured melting temperatures and the new x-ray measurements, and one can conclude that at 100 GPa, the iron melting temperature must be near 3000 K.

The only DAC measurements extending beyond 100 GPa are from Boehler (1993) to 200 GPa and Saxena et al. (1994) to 140 GPa and more recently by XRD to 130 GPa (Boehler et al., 2008). These measurements are in good agreement, and within the experimental uncertainty, indicating a melting temperature at 200 GPa near 4000 K. The estimated uncertainty in these measurements of ± 200 K at the highest pressures includes the uncertainty in the melt detection and the unknown emissivity-wavelength dependence of iron. An additional source of error comes from possible chemical reactions between molten iron and the pressure medium (e.g., Al_2O_3) in these experiments. Such reactions were previously checked by electron-microprobe analysis yielding negative results (Boehler, 1993). There is also no indication of a reaction between liquid iron and the pressure medium from recent in situ synchrotron x-ray measurements up to 130 GPa and to over 3600 K (Boehler et al., 2008).

2.22.5 Shock-Wave Measurements

In comparison with the DAC method, shock-wave experiments have the capability of accessing the phase diagram at considerably higher pressures and temperatures. Since density changes occurring in phase transitions are too small to be detected by the Hugoniot, phase transitions are generally identified in shock experiments by detecting discontinuities in the sound velocities. Because of the loss of shear strength in the liquid, the measurements of the sound velocity have been proved the most useful method for detecting the pressure and density at melting. Since temperature measurements have not been proved feasible for opaque materials, such as Fe (Yoo et al., 1993), they need to be calculated. These calculations (Boness and Brown, 1990; Brown and McQueen, 1986) depend on estimates of the specific heat and Grüneisen parameter, which for iron lead to uncertainties of order ± 500 K. Each of the diagnostic methods suffers from the possibility that the short nanosecond timescales of the shock transit may cause overshoot of the equilibrium melt pressure resulting in an overestimate of the melting temperatures. This mechanism is not well understood because in order to superheat a bulk solid, there must be a barrier to the nucleation of the melt. Appreciable bulk superheating of solids with shock waves has been observed in alkali halides (Boness and Brown, 1993; Swenson et al., 1985) and fused quartz (Lyzenga et al., 1983) and discussed by Luo and Ahrens (2003) for metals.

Shock-wave measurements of the Fe longitudinal sound speeds (C_L) and the bulk sound speeds (C_B) made in the preceding text are shown in Figure 6. Brown and McQueen (1986) reported two discontinuities in the sound velocity. One discontinuity is at 200 GPa and a second discontinuity at 243 GPa. The first was identified as the onset of a solid–solid transition and the second as the onset of shock melting. Subsequently, Nguyen and Holmes (2004) reported the onset of melting at 225 GPa. The cited temperatures in these studies of 5350 and 5100 are theoretical estimates. The two shock

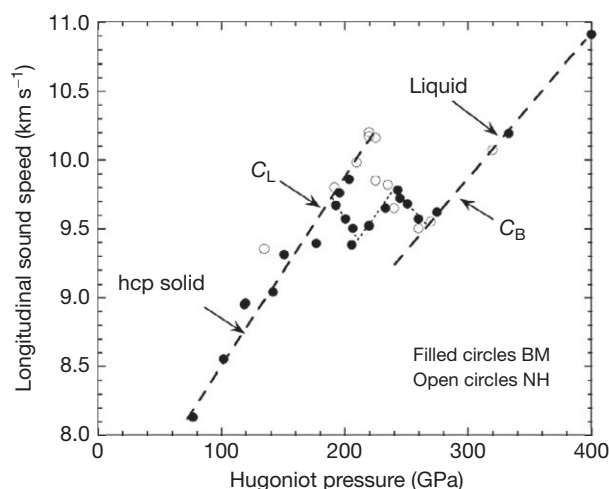


Figure 6 Shock velocity measurements by Brown and McQueen (BM) (Brown and McQueen, 1986) and by Nguyen and Holmes (NH) (Nguyen and Holmes, 2004). BM observed two transitions. Bulk melting (C_B) is observed in both experiments at about 260 GPa.

melting points are shown in comparison with Boehler's (1993) data to 200 GPa and recent theoretical estimates of the melting curve discussed later in Figure 7.

With regard to the disagreement between the static and shock melting data for iron, it is important to point out that, in general, melting temperatures measured in the LHDAC agree remarkably well with shock melting data considering the completely different nature of these experiments. Thus, problems related to kinetics, thermodynamic, and chemical equilibrium and the way temperatures are measured (static) or calculated (shock) are probably minimal. The general agreement exists for a large class of materials (alkali halides, oxides and silicates, and 'simple' metals such as Al, Cu, Sn, and Pb) (Boehler and Ross, 1997; Dewaele et al., 2007; Japel et al., 2005b; Schwager et al., 2010). However, as for iron, strong discrepancies between static measurements and shock melting exist for other transition metals such as W, Ta, and Mo (Brown and Shaner, 1983; Errandonea et al., 2001; Hixson and Fritz, 1992; Hixson et al., 1989). The extrapolated DAC data disagree with the shock melting points by several thousand degrees.

In addition to detecting phase transitions, some understanding of the material structure can be gained from a calculation of the shear modulus (G) using the density (ρ) and the longitudinal (C_L) bulk sound speeds (C_B) in the equation, $G = 3\rho(C_L^2 - C_B^2)/4$. The two sets of G s (BM and NH) are plotted in Figure 8, along with room temperature measurements of Mao et al. (1990). A third point measured by Mao et al. at a pressure of 211 GPa ($G = 396$ GPa) is beyond the range of the plotting but confirms the linearity of the low-pressure G . Starting at a pressure near 110 GPa, the values of G flatten out up to a pressure of about 210 GPa. At this pressure, the shear

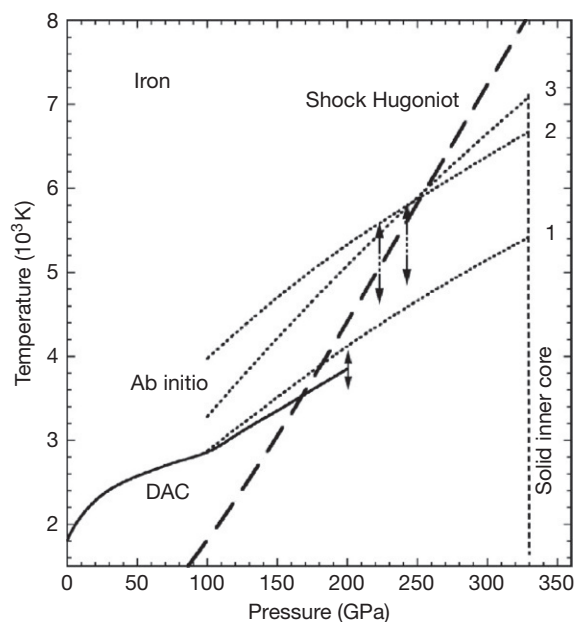


Figure 7 Comparison of iron melting curves: Diamond-anvil cell (DAC) measurements (Boehler, 1993). Shock melting experiments (see Figure 6) with reported temperature uncertainties (Brown and McQueen, 1986, Nguyen and Holmes, 2004) and from theory: 1 (Laio et al., 2000), 2 (Alfe et al., 1999), and 3 (Belonoshko et al., 2000). The differences in the melting temperatures at 3.3 Mbar (inner core boundary) are over 2500 K.

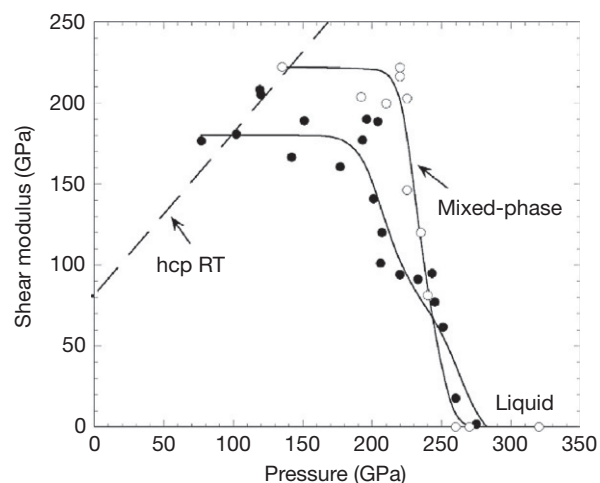


Figure 8 Iron shear modulus calculated from sound speed measurements of BM (Brown and McQueen, 1986) (filled circles) and NH (Nguyen and Holmes, 2004) (open circles). Room temperature measurements are from Mao et al. (1990) (dashed line).

modulus drops precipitously to the liquid value of $G = 0$ near a pressure of 260 GPa. Overall, this behavior resembles that of a typical elastic-plastic failure mechanism. This implies that in the shock experiments between roughly 110 GPa (2000 K) and 210 GPa (4700 K), iron is in a plastic-like state that undergoes a continuous change to a classic liquid near 260 GPa (6100 K).

Observations in melting experiments in the DAC may support this picture of plastic-like states or viscous melts from qualitative experimental observations of the melt motion using the laser speckle method: For all materials ranging from noble gases, alkali halides, oxides, and many metals, we observed that the vigor of motion strongly decreased with increasing pressure along and even far above the melting curve. Often, the disappearance of motion limited the pressure range of these melting measurements. The exact nature of this observed motion is not understood, but apart from temperature gradients, surface tension, and the strength of the pressure medium, it is likely related to the viscosity of the melt, and this could suggest an increase in the viscosity of molten iron of several orders of magnitude and that at high pressure, the liquid is a solid-like phase.

An increase in viscosity, with increasing pressure, can be explained by the presence of local structures in the melt. Experimental evidence for the presence of local structures with icosahedral short-range orders (ISROs) in stable and undercooled liquids of Fe, Ni, and Zr has been reported by Schenk et al. (2002) using a combination of electromagnetic levitation and neutron scattering. These experimental findings have been confirmed by the first-principles DFT simulations of Kim and Kelton (2007), Lee and Lee (2007), Ganesh and Widom (2006, 2008), and Di Cicco et al. (2003) using ab initio simulation methods. Since local structures are denser than the liquid average, their concentration increases with increasing pressure.

2.22.5.1 Fe Phase Diagram

A consistent picture of the Fe phase diagram, as derived from the experimental DAC and shock measurements, is described

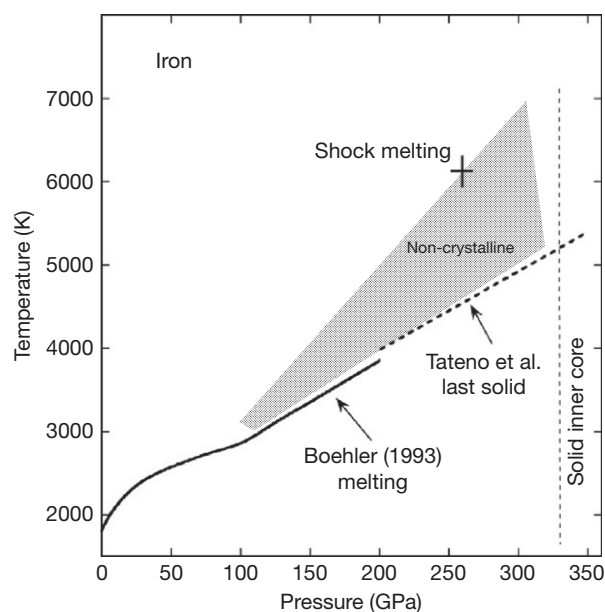


Figure 9 Iron phase diagram derived from static diamond-anvil cell work and shock melting experiments (for details, see text).

in Figure 9. Starting from ambient conditions, the liquid becomes increasingly viscous and solid-like near 100 GPa. At this pressure, Boehler found there was no longer any evidence of liquid motion, not even at temperatures exceeding the melting temperatures by several hundred degrees. Near 180–200 GPa, the Hugoniot crosses from the hcp solid to a solid-like, mixed phase (see Figures 6 and 8) to complete melting near 260 GPa (~6100 K). The liquid–noncrystalline phase boundary is sketched in starting from near 100 GPa to the shock melting point. Also indicated are synchrotron XRD experiments reported by Tateno et al. (2010). Their experiments showed ‘that the hcp structure of Fe is stable up to 377 GPa and 5700 K,’ a pressure and temperature corresponding to inner core conditions. These XRD measurements showed extensive grain growth above 3700 K, suggesting that this temperature is close to the melting point, in agreement with the extrapolated melting measurements (Boehler, 1993).

Theoretical calculations, typified by the work of Alfe et al. (2004a), have reported calculations of the hcp melting curve as shown in Figure 7. It does not agree with the experimental measurements. This disagreement has led some to doubt the validity of the measurements. We believe that the Alfe et al. calculations to predict the lower-pressure melting of hcp Fe failed to include the contribution of local structure to the lowering of the liquid-free energy. Oddly, the Alfe melting curve provides a reasonable estimate of the Fe noncrystalline solid phase. The significance of this remains unclear. Similar results have been obtained by Belonoshko et al. (2000). The results of these calculations were shown in Figure 7. Belonoshko et al. based their two-phase equilibrium calculations on model potentials fitted to quantum calculations of the Fe solid phases at 0 K, so there is no assurance that these simple potentials can reproduce correctly the electronic properties of the solid or liquid metal at extreme conditions. A more rigorous method for calculating the properties, ab initio DFT–MD,

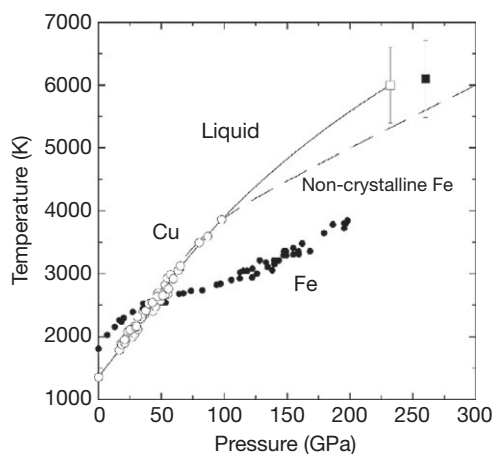


Figure 10 Comparison of the calculated melting curves for Fe (dashed curve) (Alfe et al., 2002) and Cu (solid curve) (Vocadlo et al., 2004) with the experimental DAC melting curves for Cu (open dots) (Japel et al., 2005a) and Fe (solid dots) (Boehler, 1993) and the shock melting points for Fe (solid square) (Brown and McQueen, 1986; Nguyen and Holmes, 2004) and Cu (open square) (Hayes et al., 2000).

was employed by Alfe et al. (1999, 2002, 2004a). However, the failure of these methods to predict the Fe phase diagram is the failure to include the presence of local structures in the liquid-free energy.

A comparison of the Fe and Cu measurements can provide insight to the role electronic structure plays in the phase diagram of the transition metals. Cu has a filled d-band, lying below an s-like valence band at the Fermi surface that plays no part in chemical bonding, while Fe has a partially filled d-band, with the capacity to enter into chemical bonding. Plotted in Figure 10 are the LHDAC and shock melting measurement of Fe (Boehler, 1993; Brown and McQueen, 1986; Nguyen and Holmes, 2004) and Cu [19]. A theoretical calculation of the Fe melting curve by Alfe et al. (2004a) is in excellent agreement with the Cu melting measurements. Since Fe has a partially filled 3d electron valence, it has a greater likelihood to form high-temperature, noncrystalline structures than Cu, which has a filled 3d-band and forms a plastic-like phase. In contrast to Fe, there was no evidence in Cu of an increase in the liquid viscosity over the entire pressure range over which melting was observed. This implies a lack of local structures in liquid Cu. Ganesh and Widom (2006, 2008) had found that the degree of icosahedral order in liquid Fe is greater than in liquid Cu. The good agreement of the Cu and Fe shock melting near 250 GPa (6000 K) can be attributed to a reduction of local structure in the Fe liquid resulting from the high temperature, thereby converting Fe into a Cu-like metal. The calculation of the Fe melting curve by Alfe et al. (2004b) predicts a Cu-like melting curve at all pressures because it neglects the presence of local structures.

2.22.6 Iron at the Earth's Core Conditions

Thirty years ago, Jacobs (1975) made the frequently cited statement: "The viscosity of the Earth's core is one of the least well known physical parameters of the Earth. Estimates

in the literature of the kinematic viscosity differ by many orders of magnitude, ranging from 10^{-3} to 10^{11} $\text{cm}^2 \text{s}^{-1}$." These predicted viscosities range from values measured for liquid iron at one atmosphere (similar to water, about 10^{-3} Pa s) to those of glass-like liquids (like pitch, 10^{10} Pa s). There remains even today a broad consensus that the region of the outer core, from 135 to 330 GPa, suffers from a very high unexplained viscosity (Anderson, 1980; Palmer and Smylie, 1999; Smylie, 1999; Stevenson, 1983). In order to reconcile the high core viscosities derived from various seismic observations with low liquid iron viscosities, Stevenson suggested a two-phase suspension model (solid iron or oxide particles in liquid iron) and obtained high viscosities of up to 10^{11} Pa s. Such a view appears consistent with a melt containing randomly packed ISRO clusters in liquid iron. Clearly, more experimental work on liquid structures is necessary, but the hypothesis of a highly viscous outer core is supported by the observed presence of local structures in metallic melts at elevated pressure and the qualitative experimental observations of decreased melt motion using the laser speckle method (see preceding text).

Theoretical estimates of the viscosity of molten iron at core conditions were done using several unknown thermodynamic parameters such as the activation energy (Poirier, 1988), and the low viscosities predicted have been supported by MD simulations (Wijs et al., 1998). There are, however, qualitative trends indicating an increasing viscosity of liquid iron with increasing pressure: At low pressure, there have been a number of attempts, for example, by LeBlanc and Secco (1996), to measure the viscosity of liquid iron–sulfur alloys at high pressure to a few GPa. A theoretical analysis of grain-size measurements of quenched iron liquid to 10 GPa is also indicative of a strong pressure dependence of the viscosity (Brazhkin and Lyapin, 2000). These measurements are probably not representative of core conditions, but they support the generally observed increase of viscosity with pressure such as Bridgman's early experiment on organic liquids, measurements for the noble gases (Trappeniers et al., 1980), and our own observations for liquid iron (see preceding text).

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2.23 Thermal Conductivity of the Earth

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Abbreviations

DHO	Damped harmonic oscillator
FWHM	Full width at half maximum
LFA	Laser-flash analysis

PTGS	Picosecond transient grating spectroscopy
RHTM	Remote heating thermocouple method

Symbols

ξ	Energy density	χ	Thermalization time
φ	Angle	a	Lattice constant
		A	Absorption coefficient

$a_1, b_1, c_1, \dots$	Fitting parameters	q	Wave vector
c	Speed of light	R	Reflectivity
C, c	Heat capacity	S	Radiative component
D	Thermal diffusivity	t	Time
d	Thickness or grain size	T	Temperature
F	Flux	u	Group velocity
h	Planck's constant	V	Volume
H	Heat source term	Z	Formula units in the primitive cell
I	Intensity	Λ	Mean free path
i, j, k, m	Integer indices or exponents	α	Thermal expansivity
K	Bulk modulus	ϵ	Emissivity
k	Thermal conductivity	γ	Grüneisen parameter
k_B	Boltzmann's constant	λ	Wavelength
L	Length or length scale	ν	Frequency
M	Molar formula weight	ρ	Density
n	Index of refraction	σ	Stefan–Boltzmann constant
N, x, y, z	Scalar directions	τ	Lifetime or decay constant
P	Pressure	ω	Circular frequency
Q	Contact resistance		

Subscripts

dif,rad Diffusive and radiative
lat Lattice

ph,sct Phonons and scattering

2.23.1 Introduction

2.23.1.1 The Importance of Thermal Conductivity to Geophysics

In response to a thermal gradient, heat energy in large, planetary bodies moves via five distinct processes: conduction, radiation, advection, magmatism, and outgassing. Conduction and radiation are microscopic mechanisms that only move heat. When these processes are insufficient to maintain an imposed temperature gradient, the medium as a whole moves (advection) and the flowing mass elements, each with finite temperature, carry heat according to their heat capacity. Convection is a system-wide response rather than a fundamental mechanism, including effects of conduction, radiation, and advection. Furthermore, convection can be overprinted by the two remaining processes, magmatism and outgassing, which occur at high-temperature gradients and are distinguished from advection due to much higher buoyancy contrasts and accompanying chemical differentiation (Hofmeister and Criss, 2013).

A first-order step to decipher the complex heat transfer behavior of the Earth is to quantify the two microscopic processes. Radiative transfer at high frequency is fast and is important following transient events (Hofmeister, 2010a). Slow cooling is governed predominantly by heat conduction and is quantified by thermal conductivity (k), which by Fourier's law links temperature (T) and flux (F),

$$F = -k\partial T/\partial N \quad [1]$$

where the length-scale N is normal to the surface. The temperature dependence of k is crucial, which is revealed by examining the equation for heat conduction in an isotropic medium,

$$\rho C_p \frac{\partial T}{\partial t} = k\nabla^2 T + H + \frac{\partial k}{\partial T} \left[\left(\frac{\partial T}{\partial x} \right)^2 + \left(\frac{\partial T}{\partial y} \right)^2 + \left(\frac{\partial T}{\partial z} \right)^2 \right] \quad [2]$$

where ρ is the density, C_p is the heat capacity at constant pressure (P), t is the time, and H describes heat sources such as radioactivity (Carslaw and Jaeger, 1959). The T dependence of k is complex because this is the product of three physical properties (ρ , C_p , and thermal diffusivity, D) with complex and contrasting T dependencies:

$$k = \rho C_p D \quad [3]$$

Forms and values of $k(T)$, or $D(T)$, strongly influence the temperature distribution obtained in conductive cooling models due to the nonlinear nature of eqn [2]. Examples include warming of subducting slabs, stability of olivine near the transition zone, occurrence of deep earthquakes (Branlund et al., 2000; Hauck et al., 1999; Marton et al., 2005), buckling of the lithosphere (Gerbault, 2000), and magmatic processes (Whittington et al., 2009).

Mantle convection involves competition between diffusion of heat (thermal conductivity), resistance to motion (viscosity), and buoyancy forces (thermal expansivity). Variable k has mostly been neglected in modern geodynamic studies, in view of the stronger exponential dependence of viscosity on temperature (e.g., Tackley, 1996). However, even regimes considered to be dominated by viscosity, as at high Rayleigh numbers, are impacted by variable k (Dubuffet et al., 2000) due to feedback in the temperature equation. Feedback occurs because k is a coefficient inside the differential operator of the temperature equation, which is nonlinear, much like eqn [2] for conduction. The effect of variable k on mantle convection is not overridden by simultaneously and strongly varying

viscosity (van den Berg et al., 2004; Yanagawa et al., 2005) because (1) the time dependence of an infinite Prandtl number fluid such as the mantle is primarily governed by the temperature equation and (2) the temperature equation functions as a 'master' equation, whereas the momentum equation, which is governed by viscosity, responds instantaneously as the 'slave' equation (e.g., Hofmeister and Yuen, 2007). Consequently, accurate characterization of k or D at temperature is essential in modeling planetary heat flow on any scale (Glišović et al., 2012; Jacobs and van den Berg, 2011; Schott et al., 2001; van den Berg et al., 2010; Yuen et al., 2000).

2.23.1.2 Types of Thermal Transport and Justification for Omitting Metals

The functional dependence of k (or D) on T is regulated by processes operating on small scales (Figure 1). Each process is associated with a length scale and also with a characteristic speed (over this scale) because cooling depends on time.

Transport of heat by scattering of *phonons* (quantized lattice vibrations) within each individual mineral grain ($k_{ph,sc}$) has been considered as the sole mechanism for lattice conductivity (k_{lat}). Models (e.g., Tang and Dong, 2010) and measurements of temperature versus time curves in laser-flash analysis (LFA) indicate that the characteristic speed is near that of sound over unit cell distances (Hofmeister, 2010a). Phonon scattering is fairly well understood due to a long theoretical history. However, our understanding is imperfect because much of the theoretical work rests on k and D data obtained using contact methods, which do not provide the true dependencies on T or P due to two systematic errors (contact resistance and ballistic radiation) being present and having opposing signs (Hofmeister, 2007a, 2008).

Radiative transfer is conceptually difficult because this process depends on frequency (ν), temperature, attenuation of light, and the distance over which temperature changes

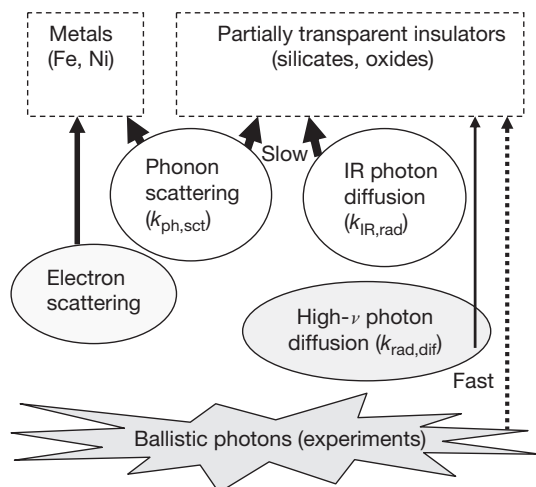


Figure 1 Types of Earth materials and associated mechanisms of heat transport. Ovals indicate mechanisms operating in the mantle. Starburst indicates mechanisms present only in the laboratory. Each mechanism has a characteristic speed, indicated schematically by arrow lengths.

significantly. For the electrically insulating mantle, wherein thermal gradients change slowly, heat can be diffused radiatively by *photons* and represented by an effective thermal conductivity, $k_{rad,dif}$ calculated from spectra. At high ν , silicate and oxide candidate minerals are transparent on millimeter scales, so diffusion consists of grain-to-grain progressive absorption and reemission of photons (Figure 2(a)). In contrast, laboratory experiments with steep temperature gradients involve a different kind of radiative transfer, termed boundary-to-boundary, direct, or ballistic (black arrows in Figure 2), wherein light from the source warms the thermocouple with scant participation of the medium (e.g., Hofmeister, 2005; Lee and Kingery, 1960). Confusion of ballistic (optically thin) with diffusive (optically thick) processes led to the misinterpretation of experimental data on minerals, both historically and recently, as detailed in the succeeding text.

In the high- ν transparent regions, the characteristic speed of diffusive radiative transfer is c/n where c is the speed of light and n is the index of refraction. This process is five orders of magnitude faster than lattice conduction, which applies over any scale, causing quasiradiative equilibrium to be rapidly attained in geologic environments. Thus, $k_{rad,dif}$ is germane to transient heating events such as core formation and magma emplacement (Hofmeister, 2010a).

In the low- ν infrared (IR) region, diffusive radiative transfer must occur, owing to the well-known equivalence of heat and light. As occurs at high ν , IR photons are absorbed and re-emitted. Unlike at high ν , the process is always diffusive because IR light is attenuated over sub-micrometer scales (e.g., Hofmeister and Bowey, 2006). However, because of their coupling with phonons, IR photons have slow speeds, like that of sound. The diffusion of IR radiation ($k_{IR,rad}$) sums

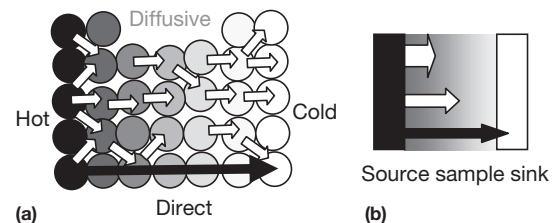


Figure 2 Schematics of high- ν photon transport mechanisms. (a) Diffusive versus ballistic radiative transfer in an internally heated medium comprised of grains. In a low-temperature gradient, each grain is effectively isothermal. The shades of the grains indicate the gradual temperature change. Diffusion (white arrows) involves emissions of photons by a hot grain, which are absorbed by the adjacent warm grains, which emit light in accord with their cooler temperatures. The net direction is the same as the temperature gradient, required by the second law of thermodynamics. Black arrows show ballistic transfer of a photon from a very hot to a very cold grain; here, no interaction with the intervening grains occurs. (b) Mixed ballistic and diffusive radiative transfer in laboratory experiments. Shading indicates the temperature gradient across a single crystal or glass. Heat from infrared (IR) photons diffuses into the medium because the intensity of IR light is increasingly attenuated with distance, indicated by the inverse correlation of arrow width and length. Ballistic transfer occurs when light (frequencies above IR fundamentals) traverses the entire sample, warming the sink (i.e., the thermocouple). Modified from Hofmeister AM (2005) The dependence of radiative transfer on grain-size, temperature, and pressure: Implications for mantle processes. *Journal of Geodynamics* 40: 51–72.

with phonon scattering to provide k_{lat} , which governs conduction (Hofmeister et al., 2014).

Heat transport in metals is relevant to planetary cores. Most geophysical studies utilize k obtained from electric conductivity (σ) using Drude's classical model (e.g., Seagle et al., 2013), which assumes that heat is transported through collisions involving electrons. However, measurements show that the ratio $k/\sigma T$ depends on temperature and do not confirm these models (Burns, 1990; for Fe and Ni metals, see Sundqvist, 1981). The experimental measurements of $k(P, T)$ for diverse metals and improvements in theoretical models needed to accurately predict heat transport at core conditions do not yet exist. Therefore, this chapter does not further discuss metals.

2.23.1.3 History of Mineral Physics Efforts and Recent Advances

Earth materials were probed in the pioneering experiments on the temperature (Eucken, 1911) and pressure response of k (Bridgeman, 1924). The seminal study of Birch and Clark (1940) found that k depends weakly on chemical composition and increases as T increases, counter to predicted behavior of phonon scattering. Assumptions that such increases represent radiative transfer led to theoretical arguments that $k_{\text{rad, dif}}$ goes as T^3 (Kellett, 1952, 1953), inference of high interior temperatures for the Earth, and thermal modeling with which Lubimova (1958) and MacDonald (1959) concluded that radiative transfer is a key process in Earth's mantle. In contrast, Preston (1956) pointed out that grain boundaries and Fe-cation content could limit radiative transfer. Evidence for plate tectonics led to the inference that mantle convection provides an efficient means for expelling heat from Earth, which made it unnecessary to call on the presence of strong radiative transfer to prevent an overly hot interior. Consequently, detailed calculations of radiative transfer for mantle minerals were limited to low-pressure materials such as olivine (e.g., Shankland et al., 1979). Issues of high interior radiative transfer have been recently revisited (e.g., Goncharov et al., 2008). However, these studies err in both incorrectly correcting baselines of the spectra and omitting grain size from the formulas (Hofmeister, 2010a).

Measurements and calculations of k in geoscience c. 1960–1980 focused on the lattice contribution, paralleling theoretical and experimental efforts in materials science (e.g., Klemens, 1958; Slack, 1979). Lithospheric processes and materials have been a continued focus (see Clausner and Huenges, 1995; Seipold, 1998; Vosteen and Schellschmidt, 2003), albeit mainly with contact measurement methods. However, fewer geologic studies were performed between 1980 and 2000 because viscosity was viewed as more important to geodynamics (Tozer, 1965).

Mineral physics research into thermal transport in the past decade was stimulated by implementation of Hofmeister's (1999) model in geodynamic models, mainly by D. A. Yuen and colleagues. The LFA technique that dominates research in materials science and engineering and lacks systematic contact losses and radiative gains (Degiovanni et al., 1994; Mehling et al., 1998) has subsequently been used to accurately constrain D in Earth science (Büttner et al., 1998). The growing database on $D(T)$ now includes diverse minerals and isostructural analogs

(e.g., Branlund and Hofmeister, 2012; Hofmeister, 2010b), glasses including above melting temperatures (e.g., Romine et al., 2012), and rocks (e.g., Nabelek et al., 2012). The large number of measurements (~ 200) on diverse materials reveals systematic behavior and suggests a new mechanism for heat transport (Hofmeister et al., 2014).

Pressure measurements that simultaneously tightly constrain P , T , and D have yet to be performed. Most measurements of D at P involve contact with thermocouples (e.g., Manthilake et al., 2011) and thus contain systematic errors from contact losses and radiative gains (Hofmeister, 2007a, 2008). Very high P measurements made with a transient technique by Beck et al. (2007) and Goncharov et al. (2009) use a geometry that precludes extracting meaningful results on lattice conduction (Hofmeister, 2008, 2009, 2010a). The most promising technique for pressure measurements is thermoreflectance (e.g., Ohta et al., 2012; Section 2.23.5).

2.23.1.4 Scope of the Original and Revised Chapters

Our present discussion concerns microscopic mechanisms of heat transfer at $T \geq 298$ K, testing them against measurements of thermal diffusivity of crystalline solids and applying them to Earth's mantle. Heat transport of glasses and melts is postponed until greater accuracy exists at temperatures well above the liquidus (see Hofmeister et al., 2009; Romine et al., 2012 for available data). The original 2007 chapter compared contact measurements of electric insulators to LFA data, focusing on single crystals, and clarified conditions needed for radiative transfer to be diffusive. A primary goal was to ascertain conditions under which contact measurements of k or D , which constitute the bulk of experimental determinations, are trustworthy. The unfortunate conclusion was that results from contact methods for geophysically important silicates and oxides systematically underestimate k or D at low T due to thermal resistance at interfaces and overestimate k at high T due to spurious radiative transfer. The original chapter summarized available theoretical models of k_{lat} and $k_{\text{rad, dif}}$, focusing on semiempirical models. Much of this is now of historical interest because the LFA database assembled since 2007 requires substantial revisions in our thinking. The revised chapter summarizes LFA data, which have been refit to a simple, three-parameter equation. We update semiempirical models, focusing on the effect of pressure, which has yet to be accurately measured.

2.23.2 Theory of Heat Flow in Minerals and Rocks

2.23.2.1 Phonon Scattering

Debye's (1914) analogy of the scattering of phonons to collisions of molecules in a gas forms the basis of all models of heat transport in electric insulators. Peierls (1929) and Klemens (1958) related lattice thermal conductivity to summations of the form

$$k_{\text{lat}} = \frac{1}{3} \frac{\rho}{M} \sum_{j=1}^3 \sum_{i=1}^{3NZ} c_{ij} u_{ij}^2 \tau_i \quad [4]$$

where M is the molar formula weight, Z is the number of formula units in the primitive unit cell, u_{ij} is the group velocity

($=d\omega_i/dq_j$), q_j is the wave vector, $\omega_i=2\pi\nu_i$ is the circular frequency of a given mode, τ_i is the mean free lifetime, $i=1-3N$ sums the normal modes of a crystal with N atoms in the formula unit, and $j=1-3$ sums the three orthogonal directions. The Einstein heat capacity of each vibrational mode,

$$c_i = \left(\frac{h\nu_i}{k_B T} \right)^2 \exp\left(\frac{h\nu_i}{k_B T} \right) / \left[1 - \exp\left(\frac{h\nu_i}{k_B T} \right) \right]^2 \quad [5]$$

is calculated per mole at constant volume, where h is the Planck's constant and k_B is the Boltzmann's constant.

All models are approximate, including those obtaining parameters from quantum mechanical formulations or molecular dynamics, because the underlying mean free gas theory is inexact. Three weaknesses exist: (1) The factor of 3 in eqn [4] is approximate (Reif, 1965). (2) Kinetic theory requires that the particles do not interact except during brief elastic collisions (e.g., Halliday and Resnick, 1966), but in fact, phonon interactions are evidenced by acoustic modes commonly appearing in IR spectra, by peak widths being finite (Lorentz's damped harmonic oscillator (DHO) model), and by overtone-combination bands occurring at lower frequencies than suggested by the fundamental frequencies and also in violation of selection rules (e.g., Mitra, 1969). Hence, greater departure from the Debye model is expected for structures that have optic modes, and successful application of the phonon-gas model to simple structures like MgO (e.g., de Koker, 2009, 2010; Morelli and Slack, 2006; Slack, 1979; Stackhouse et al., 2010; Tang and Dong, 2009, 2010) may be connected with their scant numbers of optic modes. (3) Phonon lifetimes are roughly estimated (e.g., Ziman, 1962). At high T , values of τ are assumed to go as T^{-1} (Julian, 1965; Liebfried and Schlömann, 1954; Peierls, 1929; Roufosse and Klemens, 1973), which reproduces Eucken's (1911) empirical law of $k_{\text{lat}}=B/T$ above the Debye temperature. For many materials, D becomes flat at high T . The observed deviance from $D \propto T^{-1}$ has been interpreted as arising from the breakdown of the phonon-gas model. For this reason, modern modeling efforts have considered anharmonicity (e.g., phonon interactions), which can be significant at high T (e.g., Ladd et al., 1986; Sun and Allen, 2010) but are not well constrained, even though phonon interactions violate the premise of the Debye model. To address structures more complex than can be modeled presently and materials with the geophysically important cation Fe, the semi-empirical DHO model was developed that quantifies lifetimes and their T dependence from vibrational spectra (e.g., Hofmeister, 1999), summarized in the succeeding text.

2.23.2.1.1 Pressure derivatives associated with phonon scattering

To extrapolate data on D to elevated P , we revise formula from the phonon-gas model in a manner that minimizes specifics associated with various approaches. Averaging reduces eqn [4] to

$$k_{\text{ph,scat}} = \frac{\rho}{3ZM} C_V u_p^2 \langle \tau \rangle \quad [6]$$

where the compressional velocity (u_p) pertains because the longitudinal acoustic mode involves excursions of atoms

along the direction heat propagates (Hofmeister, 2010b). The complete derivative is

$$\frac{\partial(\ln(k_{\text{ph,scat}}))}{\partial P} = \frac{1}{\rho} \frac{\partial \rho}{\partial P} + \frac{2}{u_p} \frac{\partial u_p}{\partial P} + \frac{1}{C_p} \frac{\partial C_p}{\partial P} + \frac{1}{\tau} \frac{\partial \tau}{\partial P} \quad [7]$$

To a first approximation, lifetimes depend on T only. To evaluate the heat capacity term, we use the thermodynamic identity

$$\frac{\partial C_p}{\partial P} = -\frac{T \partial^2 V}{\partial T^2} = -TV \left(\alpha^2 + \frac{\partial \alpha}{\partial T} \right) \quad [8]$$

where α is the volumetric (V) coefficient of thermal expansion. Equation [8] and data on thermal expansivity and V (e.g., Anderson and Isaak, 1995) corroborate available direct measurements on MgO (Andersson and Bäckström, 1986) and olivine and garnet (Osako et al., 2004), which provide $\partial(\ln C_p)/\partial P \sim 0.4\%/GPa$. This term is 1/10 of values of $\partial(\ln k_{\text{lat}})/\partial P \sim 5\%/GPa$ from these authors' measurements, which resemble other measurements (e.g., Beck et al., 1978; Chai et al., 1996; Gibert et al., 2003, 2005; Harrell, 2002; Katsura, 1995, 1997; Xu et al., 2004). Omitting the small but negative pressure derivatives of C_p and τ (i.e., peaks in the IR may broaden with P) provides an upper limit:

$$\left. \frac{\partial(\ln(k_{\text{ph,scat}}))}{\partial P} \right|_{\text{max}} = \frac{1}{K_T} \left(2\gamma_{\text{LA}} + \frac{1}{3} \right) \approx \frac{3}{K_T} \quad [9]$$

Equation [9] gives smaller derivatives than previous formulas, for example, those computed from the DHO model (Hofmeister, 1999, 2004) or from dimensional analysis (Dugdale and MacDonald, 1955). It is also lower than pressure derivatives obtained by Julian (1965) or of Roufosse and Klemens (1973), who associate lifetimes with the Grüneisen parameters, regardless of whether the second Grüneisen γ_{th} is approximated as ~ 1 as commonly observed (Anderson and Isaak, 1995; Knittle, 1995) or as ~ 0 , consistent with the Debye model.

Combining eqns [3] and [4], neglecting the $\sim 3\%$ difference between C_p and C_v , and using heat capacity (C_v) on per volume basis to eliminate M provide

$$D_{\text{ph,scat}} = \frac{u_p^2 \langle \tau \rangle}{3Z} \quad [10]$$

Therefore,

$$\left. \frac{\partial(\ln D_{\text{ph,scat}})}{\partial P} \right|_{\text{max}} = \frac{2}{K_T} \left(\gamma_{\text{th}} - \frac{1}{3} \right) \approx \frac{2}{K_T} \quad [11]$$

The small size of the C_p derivative and eqn [2] leads to a model-independent relation

$$\frac{\partial(\ln(k_{\text{lat}}))}{\partial P} = \frac{1}{K_T} + \frac{\partial(\ln D)}{\partial P} \quad [12]$$

2.23.2.1.2 The DHO: phonon-gas model

From the DHO model of Lorentz, the lifetime of any mode is

$$\tau_i = 1/(2\pi \text{FWHM}_i) \quad [13]$$

where FWHM_i is the full width at half maximum from individual peaks in the dielectric functions that are extracted from IR reflectivity data (e.g., Spitzer et al., 1962). Raman peaks directly

provide FWHM_i , although instrumental broadening may exist. For each mode, FWHM_i describes its interaction with all other modes in the crystal, including effects such as anharmonicity and defect scattering, and should represent an average across the Brillouin zone.

Earlier versions of the model used summations. However, due to a lack of information on dispersion relations and limitations of spectral data, averages of eqns [6] and [10] are combined with eqn [13] and are appropriate for describing transport properties.

At 298 K, the FWHM of diverse crystalline structures appears to be connected with the number of phonons within the primitive unit cell (Hofmeister, 2004). This finding is consistent with the kinetic theory of gases, wherein lifetimes are connected with number of molecules per unit volume (e.g., Reif, 1965). Also, solid solutions have lower D or k than their end-members, which is consistent with their FWHM being larger than that of either end-members (e.g., Giesting and Hofmeister, 2002).

Regarding the T derivatives, sound velocities of dense minerals depend weakly on temperature; $\partial(\ln u)/\partial T$ is near $-0.004\%/K$ for grossular and pyrope garnets and is -0.006 to $-0.008\%/K$ for forsterite and olivine (Anderson and Isaak, 1995). Raman spectra of various garnets show that peak widths increase strongly as temperature increases (Gillet et al., 1992), but this parameter was not quantified. Raman spectra show that forsterite and olivine peak widths increase strongly with T (Kolesov and Geiger, 2004a), such that $\partial(\ln \text{FWHM})/\partial T$ is near $0.14\%/K$ for three Raman peaks examined in detail. This result compares closely with quantitative analysis of IR data for MgO , which provides $\partial(\ln \text{FWHM})/\partial T = 0.25\%/K$ (Kachare et al., 1972). Thus, the temperature dependence of D is dominated by the response of FWHM. From the succeeding text and eqns [10] and [13], D_{lat} should depend inversely on T .

The pressure dependence of τ or FWHM should be small; this property is closely related to population of vibrational states, which is governed by temperature. Few relevant spectroscopic measurements exist. Raman measurements above 100 K of ZnO (Serrano et al., 2003) give $\partial \ln(\text{FWHM})/\partial P = 0$. Derivatives below 100 K from other materials are larger, $\sim 1\text{--}10\%/GPa$, but this trend could be due to the methanol-ethanol medium being stiff at lower T . It appears that $\partial \ln(\text{FWHM})/\partial P$ is small but finite above 298 K, indicating eqns [9] and [11] set upper limits.

2.23.2.2 Radiative Transport Within a Medium

Confusion and misinformation accompany analyses of radiative heat transfer of high-frequency photons within solids, in part because the ballistic type is the most familiar (i.e., light from the Sun warms the Earth's surface), whereas the diffusive type is relevant to processes inside the Earth, but is not present in experiments. We therefore begin with a general discussion.

2.23.2.2.1 Distinguishing ballistic from diffusive radiative transport

Whether radiative transfer is ballistic or diffusive depends on two length scales: that over which light is attenuated and that over which temperature changes. For any given distance in a medium over which T changes by a nontrivial amount,

radiative transfer is ballistic when conditions are optically thin (i.e., light passes through the medium) but diffusive when conditions are optically thick (i.e., light is strongly absorbed by the medium). Because electric insulators absorb some frequencies and transmit others, average absorbance cannot be used to represent photon mean free paths as is commonly assumed in geophysics (e.g., Ross, 1997). This oversimplification has led to misapplication of formulas for diffusion to situations where ballistic transfer occurs.

Based on rock samples, the average grain size in the mantle is ~ 1 mm. Back reflection of a trivial amount (0.005%) of the photons at grain boundaries due to mismatches between indices of refraction essentially extinguishes scattered light over distances of 2–200 m. This extinction length does not include absorption losses and thus holds for frequency regions with virtually no absorbance. Mantle temperature gradients are below $\sim 10 \text{ K km}^{-1}$, so light emitted from any given grain thus should not reach a neighboring grain with a temperature differing by more than 1 K, precluding ballistic radiative transfer. Grain-to-grain diffusion (i.e., absorption and reemission) of internally generated heat describes the physical process within the mantle.

The radiative process operating in laboratory experiments differs significantly from diffusion in the Earth due to the length scales over which temperature varies. Gradients are $\sim 1 \text{ K mm}^{-1}$ in experiments (Parker et al., 1961). In laboratory experiments, the transparency of the near-IR to UV regions (Figure 3) allows the emissions of the heater to cross the sample largely unattenuated, warming the thermocouple without participation of the (optically thin) medium (Figure 2). In contrast, the strong absorptions in the IR region prohibit ballistic radiative transfer of IR energy over laboratory scales but permit diffusion (discussed in the succeeding text).

The amount of light crossing the sample at any given frequency is quantified via the true absorption coefficient (A), which depends strongly on ν and thickness (d),

$$A(\nu)d = -\ln \left[\frac{I_{\text{trans}}(\nu)}{I_0(\nu)} \right] + 2 \ln[1 - R(\nu)] \quad [14]$$

where I_{trans} is the intensity of light exiting the crystal and I_0 is intensity entering the crystal. The reflectivity ($R = I_R/I_0$, where I_R is intensity reflected from the surface) term accounts for laboratory measurements being obtained from a sample with flat, parallel surfaces. For weakly absorbing spectral regions, and normal incidence, Fresnel's law is simple:

$$R = (n - 1)^2 / (n + 1)^2 \quad [15]$$

If additional scattering is present, such as from grain boundaries or imperfections, a baseline is subtracted to obtain A . Roughly, a medium is optically thin if $A(\nu)d < 1$, which allows $>36\%$ of the light through (ballistic radiative transfer). For a medium to be optically thick and the process to be considered diffusive, $A(\nu)d > 2$, in which case, $<14\%$ of the light is transmitted (Siegel and Howell, 1972).

Emission characteristics are also germane. Planck's black-body function is

$$I_{\text{bb}}(\nu) = \frac{2h\nu^3}{c^2} \left[\frac{1}{\exp(hc\nu/k_B T) - 1} \right] \quad [16]$$

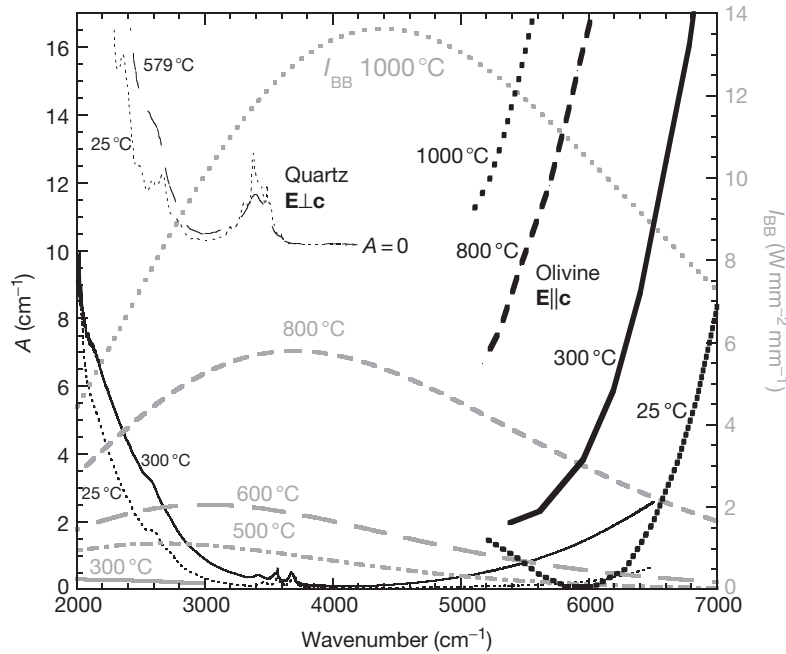


Figure 3 Temperature and frequency dependence of spectra. Black curves and left y-axis = near-IR spectra of olivine $E||c$ and quartz $E\perp c$ (left y-axis). Gray curves and right y-axis = blackbody function at various temperatures, as labeled (I_{BB}). Olivine (Fe_{90}) data = medium black lines from Hofmeister (2005) and thick lines only at higher wave numbers from Ullrich et al. (2002). Quartz data = fine lines from Aines and Rossman (1985), offset for clarity: A actually is 0 for the flat section near 4000 cm^{-1} . For temperatures accessed in contact measurements of k or D (up to $\sim 800^\circ\text{C}$), the blackbody curve occupies the transparent spectral region of Fe-free minerals and those with octahedral Fe^{2+} .

where the energy is provided on a per-frequency basis. Blackbody intensity increases about tenfold between 700 and 1000 K . The blackbody peak depends on T ,

$$\nu_{\max} (\text{in cm}^{-1}) = 3.451T (\text{in K}) \quad [17]$$

and is located in the transparent near-IR at temperatures of heat transfer experiments (Figure 3).

Measuring absolute values of A at high T is difficult (Grzechnik and McMillan, 1998). Not all reported A values include a baseline correction, and virtually all of the mineralogical literature uses common logarithms in a format analogous to eqn [14]. We account for these differences and use olivine to represent minerals with Fe^{2+} in octahedral sites because the d-d electronic transitions are largely determined by the site occupied by Fe, whereas characteristics of the overtones of the Si-O tetrahedron vary little among diverse minerals (cf. olivine to quartz near 2000 cm^{-1} in Figure 3). Similarly, quartz should represent Fe-free minerals.

For quartz, $A < 0.05\text{ mm}^{-1}$ for $3700\text{ cm}^{-1} < \nu < 4200\text{ cm}^{-1}$ from ~ 20 to 579°C , using $n = 1.55$ in eqns [14] and [15] and data from Aines and Rossman (1985). This weak absorbance is associated with overtones of hydroxyl or water, which are $\sim 1/100$ the intensity of the fundamentals present near 3500 cm^{-1} (Figure 3). The data indicate that low absorbance should persist into the visible region and to higher temperatures. Measurements of microcrystalline and milky quartz up to 700°C (Yamagishi et al., 1997) and fused silica up to $\sim 1400^\circ\text{C}$ (Grzechnik and McMillan, 1998) provide confirmation. Quartz is quite transparent ($\sim 80\%$ of the near-IR to visible flux is

transmitted across 4 mm), and ballistic radiative transfer is expected over many cm, thicknesses much larger than used in contact experiments (e.g., Gibert et al., 2005).

Olivine spectra (Figure 3) show that A is essentially negligible up to $\sim 300^\circ\text{C}$ in the transparent near-IR region. The rise at low frequency at 25°C between 5000 and 6000 cm^{-1} seen by Ullrich et al. (2002) is not supported by our results or those of Taran and Langer (2001) and may be due to low sensitivity near the limit of their spectral range. Combining all available data suggests that A is $\sim 0.1\text{ mm}^{-1}$ at 4000 cm^{-1} near 800°C and that $>50\%$ of the flux in the narrow region from ~ 3000 to 4500 cm^{-1} is transmitted for 4 mm lengths typical in heat transfer experiments. The blackbody curve at these temperatures peaks in this spectral segment (Figure 3), and thus, radiative transfer for Fe^{2+} bearing samples is largely ballistic at temperatures of up to 800°C probed in conventional methods. This inference is corroborated by temperature-time curves of millimeter thick olivine samples in the LFA experiments of Pertermann and Hofmeister (2006).

Ballistic radiative transfer being present in contact measurements is obviated by an increase in k with T above $\sim 400^\circ\text{C}$ (Figure 4). This change is associated with the strong nonlinear increase of blackbody flux in the transparent near-IR, not with involvement of Fe^{2+} absorptions, as these negligibly overlap with the blackbody curve at such low temperatures (Figure 3). That the change in $\partial k/\partial T$ for quartz, which lacks Fe^{2+} bands, occurs at a similar temperature in contact experiments (Kanamori et al., 1968) shows that ballistic radiative transfer in the near-IR governs both minerals.

Figure 5 provides a flowchart for determining whether radiative transfer is diffusive or ballistic. The amount of

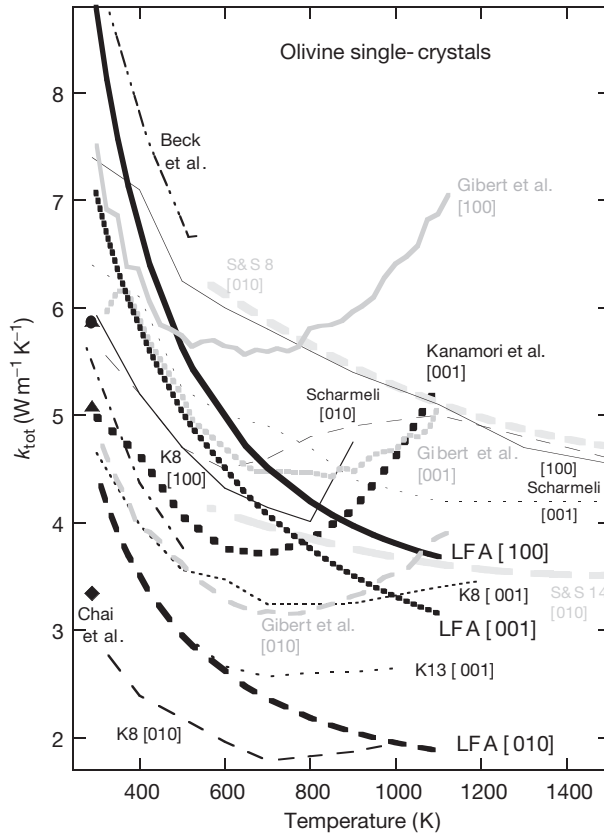


Figure 4 Literature data on the temperature dependence of the measured total thermal conductivity from single-crystal olivines. Black symbols at 298 K are the three orientations of $\text{Fe}\# = \text{Fe}/(\text{Fe} + \text{Mg}) = 0.11$ measured using picosecond transient grating spectroscopy (PTGS) (Chai et al., 1996). Solid lines = [100]; dotted lines = [001]; dashed lines = [010]. Light gray heavy lines are polynomial fits for $\text{Fe}\# = 0.08$ and $\text{Fe}\# = 0.13$ using a laser-wave method, labeled S & S (Schatz and Simmons, 1972a). Medium black lines are laser-flash data (Pertermann and Hofmeister, 2006). Medium gray lines are for a remote heating thermocouple method (Gibert et al., 2005). All other studies use contact methods. Dot-dashed lines = unknown composition and orientations of Beck et al. (1978). Small squares are (001) for $\text{Fe}\# = 0.18$ (Kanamori et al., 1968). Widely spaced dotted line labeled K13 is $\text{Fe}\# = 0.13$ (Kobayashi, 1974). Thin lines labeled K8 are the three axes for $\text{Fe}\# = 0.08$ (Kobayashi, 1974). Very thin lines are three orientations of $\text{Fe}\# = 0.08$ acquired at 2.5 GPa (Schärmeli, 1982).

ballistic radiative transfer in laboratory experiments depends on specifics such as the thickness of the sample and its absorption characteristics.

2.23.2.2.2 Spectroscopic models for grain-to-grain diffusive radiative transport

Errors exist in previous derivations for the effective thermal conductivity associated with an optically thick, nonopaque medium in local radiative equilibrium (e.g., Clark, 1957; Hofmeister, 2005; Kellett, 1952, 1953; Shankland et al., 1979). A new and independent derivation and a detailed discussion of grain size effects is provided by Hofmeister (2014a). Here, we modify recent formula to be consistent with underlying assumptions. Namely, because forward scattering dominates, rays of light

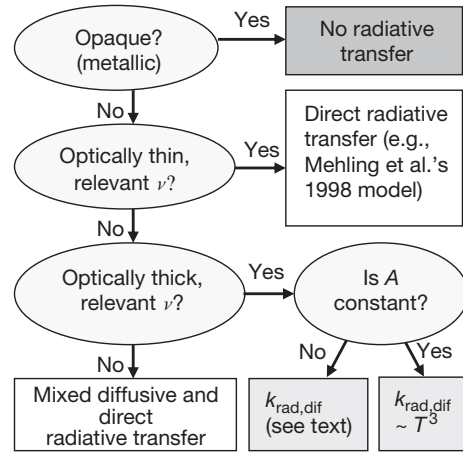


Figure 5 Flow chart for discerning whether radiative transfer is diffusive or ballistic, with links to appropriate models, discussed in the text. 'All relevant ν ' refers to frequencies up to where I_{bb} is negligible at the temperature of interest.

carrying heat propagate perpendicular to the hot interface (Figure 2), and the index of refraction should not be included. This approach is consistent with neglecting effects of grain shape and use an average grain size, as is assumed when incorporating viscous damping in geodynamic models (e.g., Ranalli, 2001).

For parallel rays, the energy density, after Hofmeister (2005, 2014a), is

$$\xi = (1 - R)\epsilon I_{bb} \quad [18]$$

where $\epsilon(v, T)$ is emissivity. Kirchhoff's law for a body in thermodynamic equilibrium requires that emissivity equals absorptivity, $a(v, T) = I_{abs}/I_0$, where I_{abs} is the light actually absorbed and I_0 is intensity entering the crystal (e.g., Bates, 1978; Brewster, 1992). Therefore,

$$\epsilon(v, T) = a(v, T) = 1 - \exp[-dA(v, T)] \quad [19]$$

The factor $(1 - R)$ in eqn [18] accounts for light being reflected at grain interfaces. However, mantle minerals have similar n values, so back reflections can be neglected to first order. Note that single-phase ceramics scatter light profusely due to porosity (due to air at grain boundaries). Mantle rocks should have no porosity due to high confining pressures and so should be more similar to ceramics prepared by spark plasma sintering, which have high optical quality even at nanometer grain size because pore spaces with air were removed during synthesis (Chaim et al., 2004).

Incorporating ϵ , neglecting n , and using the definition of the mean free path (A),

$$\frac{1}{A} = \frac{1}{d} + A(v) \quad [20]$$

provide a slight modification of the formula of Shankland et al. (1979):

$$k_{rad,dif}(T) = \int_0^\infty \left[\frac{d}{d + A(v, T)} \right] \frac{\partial}{\partial T} \left[\left(1 - e^{-dA(v, T)} \right) \frac{8\pi h v^3}{3c^2} \frac{1}{e^{(hv/k_B T)} - 1} \right] dv \quad [21]$$

2.23.2.2.3 Understanding the general behavior of $k_{\text{rad,dif}}$ from asymptotic limits

If a material is dark (dA large) and if A is essentially constant over all frequencies, then eqn [21] can be integrated from $\nu=0$ to ∞ , providing a formula similar to that of Clark (1957):

$$k_{\text{rad,dif}} \propto T^3/A \quad (\text{for } dA \text{ large and constant}) \quad [22]$$

Although these conditions are rarely met in minerals, eqn [22] describes some key features of radiative diffusion. Note that d is not explicitly contained in the formula. For an opaque medium ($A \rightarrow \infty$) and any value of d , the limit ($k_{\text{rad,dif}} \rightarrow 0$) is obtained, consistent with radiative transfer not existing in metals.

A very different result is obtained from integrating eqn [21] for nearly transparent materials with A independent of ν and T :

$$k_{\text{rad,dif}} \propto T^3 d^2 A \quad (\text{for } dA \text{ small and constant}) \quad [23]$$

Thus, as $A \rightarrow 0$, $k_{\text{rad,dif}} \rightarrow 0$. Diffusive radiative transfer is absent in a fully transparent medium because photons cannot warm the medium unless absorbed. As $d \rightarrow 0$, $k_{\text{rad,dif}} \rightarrow 0$. This case approximates exceedingly fine-grained ceramics that are effectively opaque due to back reflections. Physical scattering dominates this asymptotic limit.

The form of $k_{\text{rad,dif}}(A)$ can be inferred from eqns [22] and [23]. Because $\partial k_{\text{rad,dif}}/\partial A$ is positive at low dA but negative at high dA and both limits for k_{rad} are 0, a maximum exists in $k_{\text{rad,dif}}(A)$. The maximum is associated with moderate A and grain size, wherein physical scattering is not overwhelming, significant light is emitted by individual grains in the mantle, and this light is not completely extincted proximal to where it was emitted.

Radiative transfer is more complex than the T^3 law in eqns [22] and [23] because A depends on ν and T . However, the trend in $k_{\text{rad,dif}}$ with T can be inferred from these equations (Hofmeister and Yuen, 2007). The dependence of A on ν weakens the temperature dependence of k_{rad} as it truncates the integral of eqn [21]. For small dA , A increasing with T strengthens the temperature dependence of $k_{\text{rad,dif}}$ (eqn [23]). The effects of $A(\nu)$ and $A(T)$ roughly cancel at small dA , suggesting that for small dA , the T^3 law may be a useful approximation. But for large dA , A increasing with T decreases $k_{\text{rad,dif}}$ (eqn [22]). Dark samples are opaque over larger portions of the integral, which further decreases k_{rad} . A much weaker dependence than T^3 is expected for $k_{\text{rad,dif}}$ at high T for large dA .

2.23.2.2.4 Problems in implementing spectroscopic models of diffusive radiative transport

To avoid estimating grain size, Keppler et al. (2008), Goncharov et al. (2008), and others used Rosseland's (1936) approximation. However, Rosseland's approximation requires finite absorption at all frequencies. Because silicates and oxides are transparent over some portion of the near-IR, their approach is questionable.

The pressure dependence of $k_{\text{rad,dif}}$ is unimportant compared to temperature effects. The relevant quantity, $\partial A/\partial P = (\partial A/\partial \nu)(\partial \nu/\partial P)$, has opposite signs above and below the peak center, causing $\partial k_{\text{rad,dif}}/\partial P$ to be highly temperature-dependent, due to the peak positions and widths of A and I_{bb} both depending on T (Hofmeister, 2005). Thus, evaluating

$\partial k_{\text{rad,dif}}/\partial P$ relevant to the mantle requires near-IR spectra at simultaneously elevated P and T and cannot be determined from only $\partial \nu/\partial P$ at 298 K as previously considered (e.g., Keppler and Smyth, 2005; Ross, 1997).

2.23.2.3 Diffusive Radiative Transfer in the IR Region: A New Mechanism

Based on trends in experimental data, Hofmeister et al., 2014 proposed that absorption–emission of IR light augments scattering of phonons. For these processes to contribute equally to conduction,

$$k_{\text{lat}} = k_{\text{ph,sct}} + k_{\text{IR,rad}} \quad [24]$$

their speeds must be similar, $\sim u_{\text{p}}$, which is consistent with mixing of IR photons and phonons (e.g., polaritons; Burns, 1990; Loudon, 1970) and with dimensional analysis of time–temperature curves (Hofmeister, 2010a). Propagation of IR phonons at sound speed is also indicated by considering dispersion curves for the diatomic chain (Hofmeister, 2010b). Here, we present a simple model, based on eqn [21], to permit comparison with phonon scattering models.

From Hofmeister and Bowey (2006), absorption coefficients in the IR are $\sim 10^6 \text{ m}^{-1}$. Distances over which heat transport is measured are $>0.1 \text{ mm}$, so $\varepsilon \sim 1$ and the mean free path is governed by the absorption coefficient. The effective conductivity must be proportional to speed ($=c/n$ in the transparent region), so we insert the factor $(c/n) \times (n/c)$ in eqn [21] and then replace c/n with u_i . Using $\varepsilon = 1$ and $A = 1/A$ gives

$$k_{\text{IR,rad}}(T) = \frac{1}{3} \int_0^{\nu_{\text{max}}} \frac{u}{A(\nu, T)} \frac{8\pi c h^2 \nu^4}{k_{\text{B}} T^2} \frac{e^{(h\nu/k_{\text{B}} T)}}{(e^{(h\nu/k_{\text{B}} T)} - 1)^2} d\nu \quad [25]$$

At low T , $k_{\text{rad,IR}}$ should roughly increase linearly with T because the T dependence inside the integral is similar to a heat capacity function (shown in Figure 4 of Hofmeister, 2007b).

The factors $\Delta \nu_i$ and A_i should depend weakly on pressure because $\partial \nu_i/\partial P$ changes at about the same rate for all modes and the peak height is roughly proportional to the number of oscillators, which should not change with pressure. From this stipulation, summing over c_{Ei} , averaging the other physical properties, and using various definitions provide

$$\frac{\partial(\ln(k_{\text{IR,dif}}))}{\partial P} = \frac{1}{K_{\text{T}}} \left(3\gamma_{\text{LA}} - \frac{4}{3} \right) \approx \frac{3}{K_{\text{T}}} \quad [26]$$

where K_{T} is the isothermal bulk modulus. Nearly the same result was obtained from the DHO model for phonon scattering.

2.23.2.4 Implications of Microscopic Mechanisms Having Characteristic Speeds

All solutions to eqn [2] have the form

$$D \sim L^2/\chi \quad [27]$$

where χ is the thermalization time (e.g., Carslaw and Jaeger, 1959). Hence, the cooling front moves at a speed $u \sim L/\tau$. Inserting this approximation into eqn [27] gives

$$u \sim D/L \quad [28]$$

Over short scales, u equals that of a disturbance: the compressional velocity (u_p) for conduction (either mechanism) and c/n for high- ν photons. Regarding lattice transport for silicates, which have unit cells of $\sim 10^{-9}$ m, $D_{\text{lat}} \sim 5 \text{ mm}^2 \text{ s}^{-1}$ indicates that over a few unit cells, cooling fronts move at $\sim 5 \times 10^3 \text{ ms}^{-1}$, which is similar to acoustic velocities of $\sim 7 \times 10^3 \text{ m s}^{-1}$. These slow sound speeds hold for both mechanisms, phonon scattering and IR radiative diffusion.

Due to the simplicity of eqns [27] and [28], the ratio of the speeds at any given distance holds for all length scales. Hence, the initial response of any system (e.g., diamond anvil cell (DAC) experiments or the whole Earth) to a transient heat pulse is governed by high- ν radiative transfer because this is 10^5 faster than conduction. Quasiradiative equilibrium is rapidly attained, after which conduction governs the behavior. For this reason, $k_{\text{rad,dif}}$ plays a minor role to mantle convection or conduction across its boundary layers. Existing spectroscopic values in the literature (e.g., Goncharov et al., 2008; Hofmeister, 2005; Keppeler et al., 2008; and others) should not be incorporated in time-independent convection models for this reason, coupled with errors in the formulas used (Hofmeister et al., 2014), and high-pressure spectra contain strong, but unaccounted for, baselines (Hofmeister, 2010a).

2.23.3 Experimental Methods for the Lattice Contribution

Because $C_p(T)$ is well known (e.g., Berman and Brown, 1985), and $\rho(T)$ is fairly well constrained due to thermal expansivity being small (e.g., Fei, 1995), the temperature response of k_{lat} is readily derived from eqn [3] once $D(T)$ is known. Therefore, measurements of k or of D are effectively equivalent.

2.23.3.1 Contact-Free Methods

2.23.3.1.1 Laser-flash analysis

Accurate ($\pm 2\%$) measurements of D_{lat} for partially transparent materials can now be attained with the contact-free, laser-flash technique developed by Parker et al. (1961), due to recent advances that remove radiative transfer (Degiovanni et al., 1994; Mehling et al., 1998).

For a review, see Vozar and Hohenauer (2003). The main components of LFA are a controlled atmosphere furnace, a high-energy pulsed laser, and an IR detector (e.g., Bräuer et al., 1992). A sample in the form of a small, thin slab with parallel faces (~ 0.3 – 3 mm thick by 6 – 15 mm diameter) is held at temperature in the furnace (Figure 6, inset). Additional heat is supplied remotely to the bottom of the slab by an IR laser pulse. As the increment of heat migrates to the top of the sample, its surface temperature rises and provides an increase in emissions, which is recorded by the IR detector (Figure 6). The detector response is known as the temperature–time curve. Top and bottom surfaces of the sample are graphite-coated (thickness $\sim 1 \mu\text{m}$) to absorb laser light, thereby shielding the detector, to enhance intensity of the emissions (e.g., Blumm et al., 1997), and to buffer oxygen fugacity to C–CO, preventing oxidation of Fe^{2+} . The use of metal coatings is discussed in

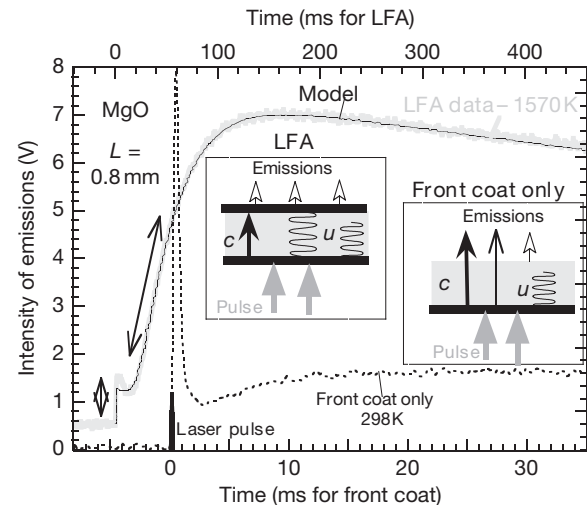


Figure 6 Raw data from laser-flash analysis (LFA) and front coat only experiments of Beck et al. (2007) and connection with microscopic processes. Gray curve = LFA time–temperature curve for MgO at 1570 K. Fine line = Mehling et al.’s (1998) model, which accounts for ballistic transfer across the sample (solid double arrow), diffusion of phonons (dotted double arrow), and ballistic radiative reequilibration with the surroundings, after either light or heat from the laser pulse reaches the top surface (open-ended double arrows). The initial pulse is drawn by the black arrow at $t=0$; the arrow width depicts pulse width. (Inset in middle) Physical transfer of heat during the experiment. A plate-shaped sample (gray) is coated top and bottom with first gold and then graphite and held at some given temperature in a furnace. Emissions (light arrows) from the top coat are recorded by an IR detector, giving a baseline. The laser pulse (heavy gray arrows) is absorbed by the bottom graphite coat. Heat from the bottom coat then traverses the sample either as photons (medium arrow) near light speed, c/n , seen in the temperature–time curve as a double arrow labeled c or as phonons and polaritons (squiggle arrow) near sound speed, u , which appear as double dotted arrow in the temperature–time curves. Bottom dotted curve = emissions from MgO when only the front is coated heavy line = laser pulse. (Inset on right) Because a back coat is lacking, light from the front Pt coat is shed directly to the detector and is strong compared to emissions from the uncoated back of the sample (open arrow). Reproduced from Hofmeister AM (2010) Scale aspects of heat transport in the diamond anvil cell, in spectroscopic modeling, and in Earth’s mantle. *Physics of the Earth and Planetary Interiors* 180: 138–147. <http://dx.doi.org/10.1016/j.pepi.2009.12.006>.

the succeeding text. Neither thermocouples nor heater contacts the sample. Equations used for data analysis require that the pulse width be significantly shorter than the time heat takes to cross the sample, which is met (Figure 6). Because the rise in sample temperature associated with the pulse is small, ~ 4 K, D is approximately constant during data acquisition, and the T dependence of D is determined by varying furnace temperature (Parker et al., 1961).

Characteristic speeds differing for radiation and conduction permit separation of the lattice component from unwanted ballistic radiative transfer. Phonon heat transfer and photon heat transfer are visually discernible in the temperature–time curves (Figure 6) and are extracted using the mathematical model of Mehling et al. (1998). This formulation for optically thin conditions accounts for absorbance being frequency-dependent, although values of optical properties are not

needed. Blumm et al. (1997) established model accuracy by comparing D calculated by applying Mehling et al.'s (1998) model to measurements of glass coated with graphite only (which has some radiative transfer) to D calculated by applying Cowan's (1963) model (see succeeding text) to measurements of the same glass, for which radiative transfer was suppressed by first applying an Au metal coating (Degiovanni et al., 1994) and then overcoating with graphite as in Figure 6, inset.

For the simplest case of adiabatic heating, without any radiative heat transfer,

$$D = 0.1388L^2/t_{\text{half}} \quad [29]$$

where L is sample thickness and t_{half} is half of the time required for temperature to reach the maximum after the laser pulse (Parker et al., 1961). Sources of experimental uncertainty in laser-flash measurements are implicit in simple models for temperature–time curves arising from phonon transport alone (e.g., opaque samples or very low temperatures). The strong dependence of D on thickness remains the main source of uncertainty. The reliability of each data point is ensured by requiring that calculated and measured temperature–time curves match. Accuracy for the technique is $\sim 2\%$, determined through benchmarking against metals and graphite (Blumm and Opfermann, 2002). These opaque and soft materials lack radiative transfer and have good thermal contact, allowing calibration against results from conventional methods for standard reference materials (e.g., Henderson et al., 1998a,b).

High accuracy requires that (1) effects of ballistic radiative transfer be removed, which is a recent advancement and not always undertaken, and (2) samples must be thin. Temperature differences larger than ~ 4 K will develop across overly thick samples during the laser pulse and thereby violate the nearly isothermal conditions assumed in the analysis. Samples with low D require very thin plates. For example, D being $\sim 2 \text{ mm}^2 \text{ s}^{-1}$ requires a thickness to diameter ratio of $1/8$ (e.g., Pertermann et al., 2008).

2.23.3.1.2 Additional optical techniques focused on pressure determinations

Picosecond transient grating spectroscopy (PTGS) has provided thermal diffusivity at ambient conditions and at ~ 5 GPa (e.g., Chai et al., 1996; Harrell, 2002). In brief, laser pulses with wavelength $\lambda = 532$ nm crossing at an angle 2φ are used to create an interference pattern with grid spacing $d = 0.5\lambda/\sin \varphi$. The signal decays as $\exp(-2t/\tau)$ where τ is a decay constant. These parameters are related to a radiative component (S) via

$$\frac{1}{\tau} = S + \frac{4\pi^2 D}{d^2} \quad [30]$$

The decay is measured by the Bragg diffraction of a third laser pulse. A concern is whether long-lived electronic states participate, in which case D calculated will be less than the true value (Chai et al., 1996). Results for olivine are $\sim 25\%$ below D from laser-flash data (Figure 7). We suggest an underlying problem in coupling of d–d electronic transitions of Fe^{2+} with lattice vibrations.

Thermoreflectance was applied to MgSiO_3 and $\text{Mg}(\text{OH})_2$ at pressure in a DAC (Ohta et al., 2012; Yagi et al., 2011). As in LFA, heating is applied remotely and detected remotely, but

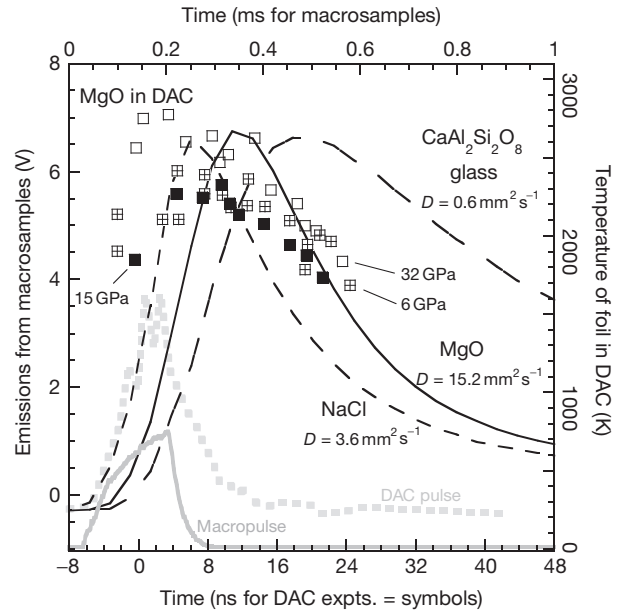


Figure 7 Time–temperature curves for samples with only the front surface coated. Solid curve = expanded view of only front coated experiments on MgO of this figure. Dashes = NaCl. Dot-dashed = glass. Curves referring to upper and left scales, compared to the diamond anvil cell (DAC) study of front coated MgO (Beck et al., 2007; Goncharov et al., 2009), shown as symbols labeled with the pressures, and referring to the lower and right scales. Gray = laser pulses (arbitrary intensity). The x-axes were scaled so that the laser pulses with and without the DAC have similar widths and the y-axes were scaled so that peak heights for the MgO samples matched. The initial rise of the emissions depends on time, due to pulses arriving over a finite time span. The fall of the emissions depends not on D of the medium/sample, but on its spectral characteristics: that is, cooling is fastest for the transparent (NaCl) sample and slowest for the most absorbent (a silicate glass). Reproduced from Hofmeister AM (2010) Scale aspects of heat transport in the diamond anvil cell, in spectroscopic modeling, and in Earth's mantle. *Physics of the Earth and Planetary Interiors* 180: 138–147. <http://dx.doi.org/10.1016/j.pepi.2009.12.006>.

samples are coated with a thin Pt-metal film instead of graphite, and reflections, not emissions, are monitored as a function of time. The raw data are initially processed to allow for thermal effusion into the NaCl pressure medium, and then, a three-layer model is applied to extract D of the sample. Values for D of Pt at pressure are presumed from data on other metals at pressures of $\sim 1\%$ of those measured (Ross et al., 1984). Ambient pressure values are used for NaCl by Yagi et al. (2011), although for this highly compressible material, D changes about a factor of four times more rapidly with P than does D of silicates (eqn [8]). A fitting parameter was used to describe heat flow into NaCl by Ohta et al. (2012). Uncertainties are estimated as $\sim 30\%$ for D by Yagi et al. (2011) but as $\sim 10\%$ by Ohta et al. (2012). Results of this technique were not benchmarked against a standard. Thermoreflectance is a transient technique, and therefore, radiative transfer can affect the initial response of the system, especially for $\text{Mg}(\text{OH})_2$, which is transparent in the mid-IR (e.g., Hofmeister and Bowey, 2006). Section 2.23.5 discusses these data in detail.

Other all-optical techniques exist, but have not been implemented in Earth science. A contact-free method for pressure

studies was developed by Pangilinan et al. (2000) but this method has large uncertainties. Optical heating and magnetization thermometry developed for low temperatures by Hao et al. (2004) has promise.

Additional measurements and benchmarking are needed to understand conditions under which reliable pressure derivatives are generated. Although some of the previous optical methods may not give absolute values of D or k , providing accurate P derivatives would be useful.

2.23.3.1.3 Problematic optical techniques

Schatz and Simmons (1972a,b) developed a time-varying, quasi-steady-state technique that is contact-free for measurement of $k(T)$. The sample is maintained at temperature in a furnace, and a CO₂ laser applies an additional oscillating heat input to one side of the sample. Heat emitted from the opposite side is monitored with a near-IR detector. Samples were not coated, so laser throughput and ballistic radiative transport contribute to k . The T^3 formula for k_{rad} is used, which presumes optically thick conditions at all frequencies (Figure 5). In contrast, optically thin conditions exist (Figure 3), so the technique of Schatz and Simmons does not constrain conduction.

The experimental configuration (Figure 7) used by Beck et al. (2007) and Goncharov et al. (2009) precludes quantifying conduction across their samples for several reasons (Hofmeister, 2008, 2009, 2010a). In these DAC experiments, the back of a thin IR metal foil is heated by a laser and emissions from its front surface are monitored by a remote detector. The front surface of the foil is against the sample. Temperatures of ~2000–2500 K are reached, so the associated blackbody curves lie in the near-IR, where the thin (10 μm) and transparent samples (MgO or salts) negligibly absorb. Shapes of their emission curves with time are characteristic of ballistic radiative reequilibration of the heated metal foil with the surroundings (cf. Cowan, 1963; Parker et al., 1961), not of conductive cooling. The time duration confirms that light speeds govern the change in emissions (Hofmeister, 2009, 2010a).

Due to high transparency of the materials, the technique only monitors heat leaving the Pt foil that does not interact with the sample or diamonds. The authors define the relevant length scale for conduction in their analysis, which determines the outcome, as exemplified by eqns [27]–[29].

Goncharov et al. (2009) dismissed radiative transfer based on the flux. Flux arguments do not negate the geometrical constraints and are not germane because these require that both phonons and photons *diffuse* and steady-state conditions exist, none of which are met in such transient experiments. Due to $\sim 10^5$ greater speeds, ballistic radiation is the only process probed in these short-term experiments. These measurements are far too brief to probe phonon transport in the samples. For further discussion, see Hofmeister (2010a). Rather, in these far-from-equilibrium DAC experiments, wherein the duration of the pulse (FWHM ~ 8 ns) is similar to ~ 30 ns measurement times, the emissions monitor the response of the foil to the laser input.

For the diverse reasons given in the preceding text, values of k_{lat} from Beck et al. (2007) and Goncharov et al. (2009) and related studies are erroneous. Problematic results associated with these methods and those of Schatz and Simmons (1972a,b) are not discussed further.

2.23.3.2 Conventional Techniques Involving Physical Contacts and Direct Heating

Many studies of $k(T)$ or $D(T)$ in Earth science utilize conventional techniques wherein a heat source and/or thermocouples directly contact the sample. Tye (1969) and Somerton (1992) described various contact methods in detail. Common features are being limited to ~ 1200 K, long measurement times, and radiative heat losses from the surface. To determine k , steady-state methods are generally used, which require information on both the flux and the temperature gradient (eqn [1]); also, boundary conditions and sample geometry influence the results. Obtaining D involves transient methods wherein the time that a thermal disturbance takes to travel a certain distance is measured. Some techniques provide both k and D (the transient hot wire and hot strip methods with uncertainties of $\pm 6\%$ and 30% , respectively; Hammerschmidt and Sabuga, 2000).

Although a large database on minerals at ambient conditions (Horai, 1971) was created using the needle-probe method, wherein k is determined from a powder (grain size < 50 μm) dispersed in water, most studies of D of Earth materials at high T use Ångström's method or its variants. In brief, a sinusoidal source of heat at frequency ω is applied to one end of a rod-shaped sample, and the phase of the decaying sinusoidal temperature wave that passes into the sample is measured at a distance L along the rod. Solutions to Fourier's equation in one dimension show that the phase depends on $L(\omega/2D)^{1/2}$. Correction terms address boundary conditions such as surface losses via radiation to the surroundings. Thermocouple attachment involves drilling a hole in the center of the sample and inserting a smaller diameter wire (Xu et al., 2004).

For hard solids, conventional measurements commonly differ by $\pm 20\%$ even at room temperature (Ross et al., 1984). For olivine single crystals with $\text{Fe}/(\text{Fe} + \text{Mg}) \sim 0.1$, discrepancies nearing 50% are seen at 298 K (Figure 4). Offsets between various data sets are consistent up to 500 – 700 K, whereupon $\partial k/\partial T$ changes sign. Trends are less regular at higher T .

Errors in results from conventional methods are partly due to variable amounts of unwanted, ballistic radiative transfer, as seen by an increase in $k(T)$ at higher temperatures. Particulars of the experiments (e.g., contact adhesives, sample thickness, and absorption characteristics) likely cause of the variation in the position and degree of the upturns in $k_{\text{meas}}(T)$. Radiative effects are reduced for small grain size or strong near-IR absorptions (e.g., Fe-rich garnet). Some researchers attempt to separate phonon from photon components by subtracting either $k_{\text{rad,dif}} \sim cT^3$ or the results of Shankland et al. (1979) from the measured k to obtain k_{lat} (e.g., Schärmeli, 1982). This approach is invalid because optically thick conditions (Figure 5) are not met in the near-IR region in experiments (Figure 3).

An additional source of error arises from systematic losses that occur in conventional measurements due to thermal contact resistance (Fried, 1969). This impediment can be described as a thermal resistance, Q , which is the inverse of the thermal conductivity of the interface. Thermal resistances add

$$\frac{1}{k_{\text{meas}}} = \frac{1}{k_{\text{sample}}} + Q \quad [31]$$

(Carslaw and Jaeger, 1959), and thus, contact measurements set a lower limit on k at 298 K, in the absence of other

problems. Differential thermal expansion between thermocouples and sample can make Q temperature-dependent. To quantify, consider the related formula:

$$D_{\text{meas}} \sim D_{\text{true}} / (1 + D_{\text{true}} / D_{\text{contact}}) \quad [32]$$

(Hofmeister, 2010b). Copper with $D = 111 \text{ mm}^2 \text{ s}^{-1}$ is commonly used. Because D of the contact (the interface) is a blend of the two substances, it will lie between D of the metal and the insulator ($D_{\text{contact}} \sim 50 \text{ mm}^2 \text{ s}^{-1}$), and the loss should be $\sim 10\%$ per contact for silicates.

Pressure derivatives of k obtained for hard solids using contact methods are uncertain due to contact losses and radiative gains (Section 2.23.3.4). If deformation alters the geometry and cracking reduces thermal contact, then values for $\partial(\ln k)/\partial P$ are unreliable, as evidenced by threefold variations between studies (Alm and Bäckström, 1974; Bäckström, 1977; Brydsten et al., 1983; Ross et al., 1984). Some uncertainties are due to pressure determinations and nonhydrostatic conditions in the older works. The two-strip method (Andersson and Bäckström, 1986; Osako et al., 2004) is the most accurate of the contact techniques used at pressure. However, most geoscience studies use variations of Ångström's method (e.g., Manthilake et al., 2011; Xu et al., 2004). Such studies have uncertainties in k of ~ 20 – 30% .

2.23.3.3 Hybrid Methods

Schilling (1999), Höfer and Schilling (2002), Gibert et al. (2005), and Marquardt et al. (2009) developed an approach in which heat is applied remotely (flux from a filament), but the sample is in contact with thermocouples, denoted RHTM (remote heating thermocouple measurement). Systematic errors associated with contact methods (contact resistance and spurious radiative transfer) also affect RHTM.

Similar to LFA, the raw data consist of the change in temperature as a function of the time subsequent to the applied heat (light) pulse. Finite difference calculations are used to determine D from the temperature difference across the sample by assuming (1) that a constant describes the heat loss from the surface and (2) that ballistic radiative transfer is proportional to the heat from the pulse, that is, absorbance is assumed to be independent of frequency or temperature. These equations assume instantaneous application of heat. Unlike LFA, the pulse width is very large, about $1/3$ of the time taken for heat to traverse the sample; thus, radiative transfer is incompletely removed by the finite difference calculations, as concluded by the authors. Höfer and Schilling (2002) and Gibert et al. (2005) tried to account for the remaining contribution of radiative transfer by assuming forms for each of the phonon and photon components (specifically, $D_{\text{lat}} = 1/(b_1 + b_2 T)$ and $D_{\text{rad}} = b_3 T^3$). This approach is invalid for several reasons. The T^3 law (Clark, 1957) describes the effective thermal conductivity, not diffusivity. Not only is diffusive radiative transfer unlikely due to transparency in the near-IR, but also the T^3 form for k is inappropriate for minerals in general and for Fe^{2+} -bearing olivine in particular (Section 2.23.2.2). Stated uncertainties of 5% rest on comparing results of Höfer and Schilling (2002) with contact measurements (e.g., Kanamori et al., 1968) that also include spurious radiative transfer and contact resistance effects.

The 3ω method (e.g., Cahill et al., 1992) also involves a single contact. Thermal conductivity is determined below $\sim 300 \text{ K}$

using a third-harmonic detection scheme from the self-heating of a narrow metal line deposited on the sample. This radial method mixes two polarizations. An important advantage is insensitivity to blackbody radiation. This technique has been used at pressures up to 0.8 GPa (Chen et al., 2004), but not on Earth materials.

2.23.3.4 Contact Losses and Radiative Gains Associated with Contact Methods

When the original version of this chapter was written, few LFA data, from which radiative effects were removed, existed for minerals. Comparisons with other techniques were made using single-crystal data, focusing on the few minerals (olivine, quartz, and NaCl) for which multiple measurements were made. We showed that contact losses and spurious radiative gains in methods using physical contacts were significant.

The LFA database has grown to include most of the common rock-forming minerals (quartz, olivine, garnet, clinopyroxene, orthopyroxene, spinel, and feldspars) plus the B1 and perovskite structures thought to be present at high pressure, as well as rocks, glasses, and melts (tabulated and examined in Section 2.23.4). Comparisons made in these latter studies confirm the earlier findings. Therefore, the remainder of this section includes the most important of the aforementioned comparisons in graphical form, but not tabulated results on contact studies from the original chapter, given that the uncertainties in these methods are $\sim 20\%$, not 5% as commonly stated.

2.23.3.4.1 Ambient conditions: contact losses overwhelm radiative gains for silicates

At 298 K, D depends on the number of thermal contacts (Figure 8). Lee and Hasselman (1985) reached a similar conclusion by replacing the detector in LFA experiments with a thermocouple. Average losses are $\sim 10\%$ per contact for silicates. Discrepancies between LFA and contact measurements are less for gemmy single crystals studied by Slack (1962, 1964) because ballistic radiative transfer is larger in more transparent materials. This deduction is supported by comparing contact data to LFA on alkali halides, which are also highly transparent, but due to low IR frequencies (Yu and Hofmeister, 2011). For most alkali halides, ballistic transfer more than offsets contact losses (Figure 9). Scatter in the plot is partly due to some authors attempting to correct contact results for high radiative transfer (e.g., by $\sim 30\%$ for LiF; Berman and Brock, 1965).

2.23.3.4.2 Elevated temperature: radiative gains overwhelm contact losses

Thermal conductivity of olivine single crystals decreases steeply from ambient temperature values (Figure 4). Initial slopes ($\partial k/\partial T$ or $\partial D/\partial T$) are nearly parallel, but as temperature increases to about 600 K, slopes from conventional methods and RHTM become less steep compared to laser-flash results. By $\sim 800 \text{ K}$, contact studies have positive $\partial k/\partial T$. Radiative transfer must be present at low temperature because (1) a small radiative component is clearly seen by $\sim 350 \text{ K}$ in time-temperature curves from LFA experiments and (2) Figure 9 shows that this effect occurs at 298 K in proportion to sample transparency. The amount of ballistic radiative transfer depends on experimental

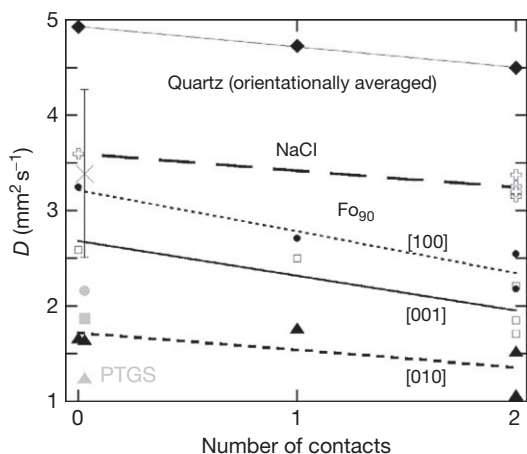


Figure 8 Thermal diffusivity at 298 K as a function of the number of physical contacts with heaters and/or thermocouples. Lines are least squares linear fits. Dot, square, and triangles = [100], [001], and [010] orientations of olivine (Table 1). Diamonds = weighted directional average of quartz (Table 1). PTGS measurements of olivine (gray) have problems other than contact; see text. Plus sign = NaCl (Brydsten et al., 1983; Håkasson and Andersson, 1986; Håkasson et al., 1988; Pierrus and Sigalas, 1985), averaging to $D = 3.25 \text{ mm}^2 \text{ s}^{-1}$. LFA results of $D = 3.6 \text{ mm}^2 \text{ s}^{-1}$ are the average of ten measurements on a crystal purchased from IR Crystal Laboratories. X = NaCl from Pangilinan et al. (2000). Reproduced from Hofmeister AM (2007c) Pressure dependence of thermal transport properties. *Proceedings of the National Academy of Sciences* 104: 9192–9197.

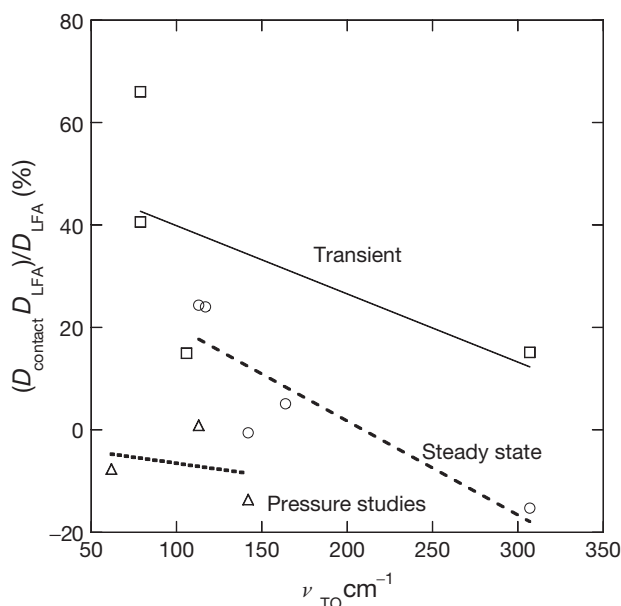


Figure 9 Dependence of the difference of D_{298} between contact and LFA methods on vibrational frequency for alkali halides. Open symbols compare various types of contact measurements to single-crystal LFA data. Solid symbols compare various types of contact measurements to pressed pellets LFA data. Square = transient contact methods. Circle = steady-state contact method. Triangle = contact measurements at high pressure on pressed powders. These are compared to LFA studies of both crystals and pressed pellets. Reproduced from Yu X and Hofmeister AM (2011) Thermal diffusivity of alkali and silver halides. *Journal of Applied Physics* 109: 033516. <http://dx.doi.org/10.1063/1.3544444>.

details such as transparency in the IR and near-IR, sample thickness, physical scattering, and temperature gradient.

2.23.3.4.3 Elevated pressure: contact losses and radiative gains persist

The accuracy of D from multianvil contact measurements is evaluated by comparing results of Xu et al. (2004) for olivine to LFA data. At high T , $\partial D / \partial T$ is similar to that from laser-flash measurements (Figure 10). However, extrapolation to 1 atm provides D similar to those of the [010] axis, which is the orientation with the lowest value but should instead nearly equal the average of the three orientations. At 400 K, the average of the single-crystal measurements is $1.69 \text{ mm}^2 \text{ s}^{-1}$, and Xu et al.'s (2004) values are below this by $0.61 \text{ mm}^2 \text{ s}^{-1}$ (36%). At 1000 K, the average of the single-crystal measurements is $0.77 \text{ mm}^2 \text{ s}^{-1}$, and Xu et al.'s (2004) values are below this by $0.20 \text{ mm}^2 \text{ s}^{-1}$ (33%). Either contact resistance is temperature-dependent or some ballistic transfer exists. Based on our comparison, $\sim 33\%$ uncertainty is associated with Xu et al.'s (2004) technique and therefore with recent measurements of perovskite structure minerals (Manthilake and de Koker, 2011; Manthilake et al., 2011).

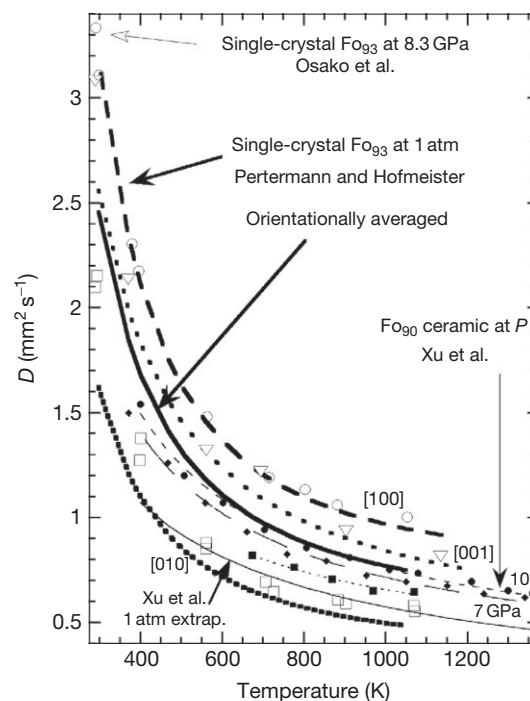


Figure 10 Comparison of contact measurements of D for olivine aggregates (filled symbols: Xu et al., 2004) and single crystals (open symbols: Osako et al., 2004), both at P and T , to 1 atm single-crystal data from LFA (heavy broken lines: Pertermann and Hofmeister, 2006). Heavy solid line = average of LFA oriented values at 1 atm. Open circles = [100]; open triangles = [001]; open squares = [010]. Thin broken lines show fits of Xu et al.'s (2004) data to $D = a + b/T$ with residual = 0.99. Dot = 10 GPa; diamond = 7 GPa; square = 4 GPa. Thin solid line = extrapolation from high-pressure fits of Xu et al. (2004) to $D = 1/T^2$ to 1 atm. Reproduced from Hofmeister AM (2007c) Thermal diffusivity of aluminous spinels and magnetite at elevated temperature with implications for heat transport in Earth's transition zone. *American Mineralogist* 92: 1899–1911.

For single-crystal olivine in DAC experiments, $D(T)$ at 8.3 GPa (Osako et al., 2004) nearly coincide with LFA results at 1 atm (Figure 10), whereas dunite $D(T)$ at 10 GPa (Xu et al., 2004) match the average of the LFA curves. Slight radiative transfer is evident in [010] above 800 K (Figure 10), which suggests that lesser amounts affect [001] and [100] of Osako et al. (2004). Because radiative transfer offsets contact losses, this comparison corroborates that contact losses exist in DAC experiments.

Similarly, $D(T)$ curves from single-crystal almandine at high P in the contact experiments of Osako et al. (2004) are parallel to LFA results at 1 atm and low T , but some radiative transfer is evident in the trend of D with T above 800 K (Figure 10). Garnets with Fe^{2+} absorb light near 5000 cm^{-1} (e.g., Manning, 1967), which suppresses ballistic transport, but the samples of Osako et al. (2004) are thin enough ($\sim 0.35 \text{ mm}$) to transmit light. Hence, in the DAC measurements of garnets, contact losses and (reduced) ballistic gains roughly cancel.

2.23.3.4.4 Are pressure derivatives in contact measurements reliable?

Pressure derivatives from contact methods depend strongly on whether the derivative is obtained by comparison to data at ambient or slightly elevated pressure as well as on the maximum pressure attained (Figure 11). The latter is an experimental artifact, because the expected change of

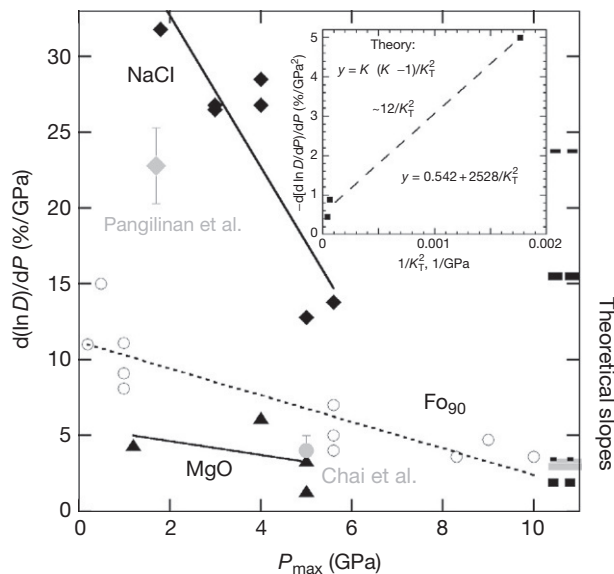


Figure 11 Dependence of pressure derivatives on maximum pressure reached in experiments on multiply studied solids. We excluded samples that cracked. Gray indicates optical methods other than LFA. Horizontal lines at left are theoretical values eqn [1]: heavy dashed = NaCl; gray = olivine; thin dashed = MgO. Sources are tabulated by Hofmeister (2007a) and the original chapter. Reproduced from Hofmeister AM (2008) Inference of high thermal transport in the lower mantle from laser-flash experiments and the damped harmonic oscillator model. *Physics of the Earth and Planetary Interiors* 170: 201–206.

$$\left. \frac{\partial^2 (\ln D_{\text{ph, sct}})}{\partial P^2} \right|_{\text{max}} \approx \frac{-2}{K_T^2} \frac{\partial K_T}{\partial P} \approx \frac{-8}{K_T^2} \quad [33]$$

is 1/400 of that observed. Progressive compression alters the interface, that is, better thermal contact occurs when the sample is under pressure because metal is highly ductile compared to silicates and oxides. Compression closes pores in polycrystalline samples as well; low-pressure studies of rocks are especially impacted. The linear trends in Figure 11 suggest that the available measurements overestimate intrinsic pressure derivatives.

2.23.4 The LFA Database on Lattice Transport for Geomaterials

At this point, the T dependence of D has been measured for ~ 200 mineral and rock samples, using LFA for which spurious radiative transfer effects have been removed. Table 1 provides our most reliable and accurate data sets on ~ 50 large single crystals with minimal fractures with geophysically relevant olivine, garnet, orthopyroxene, clinopyroxene, quartz, feldspar, spinel, B1 = MgO, corundum, and perovskite structures. Some polycrystals are included due to the importance of these compounds. Figure 12 provides examples of fits. More examples are shown by Hofmeister et al. (2014).

2.23.4.1 Thermal Diffusivity of Single Crystals

Almost all LFA data on crystalline materials are represented by a simple three-parameter fit:

$$D_{\text{lat}} = c_1 T^{-c_2} + c_3 T \quad [34]$$

Exceptions are discussed in the succeeding text. Table 1 lists our best data sets, which include gem-quality silicate minerals with solid solutions and optical flats. Similar fits are obtained for lower-quality samples, that is, those with fractures or small samples that may violate one-dimensional heat flow via edge effects.

For two cases, the $c_3 T$ term is not needed. Compounds with the B1 structure could be fit simply by $c_1 T^{-c_2}$ (Table 1; Yu and Hofmeister, 2011). In part, this simple fit exists because the halide data were acquired over a relatively small T range, which mostly does not permit extracting c_3 . However, this form fits MgO, for which data were collected to high temperature. The B1 structure has only the triply degenerate IR mode and three acoustic modes, so MgO should have a large acoustic contribution (Tang and Dong, 2009, 2010) compared to silicates for which acoustic modes are only a few percent of the total modes. Minerals in the spinel family are known to disorder as T increases (e.g., Millard et al., 1992), which lowers D and thus offsets the $c_3 T$ term. In addition, hercynites have Fe in both 2+ and 3+ states. As T increases, both Mg–Al exchange and oxidation/reduction could affect D . Note that synthetic spinel, which was disordered before heating, has a large c_3 term (Table 1).

Equation [34] accurately and simply represents LFA data of partially transparent insulators, noting that measurements at T above $\sim 900 \text{ K}$ are needed to for accurate determination of c_3 and that exceptions are connected with disordering or very few IR modes.

Table 1 Thermal diffusivity fits to single crystals and select polycrystals

Sample	Simplified formula	D_{298} ($\text{mm}^2 \text{ s}^{-1}$)	$D(T)$	$T_{\text{fit,max}}$ (K)	χ^2
Xenocryst ^{a,b}	$\text{Py}_{71}\text{Al}_{15}\text{Sp}_{60}\text{Gr}_{12}\text{An}_0\text{Uv}_2$	1.17	$230(62)T^{-0.951(48)} + 0.00040(3)T$	920	0.002
Rhodolite	$\text{Py}_{56}\text{Al}_{37.9}\text{Sp}_{0.8}\text{Gr}_{5.3}\text{An}_0\text{Uv}_0$	1.22	$67.5(12.0)T^{-0.717(32)} + 0.00024(2)T$	950	0.003
Py-Al	$\text{Py}_{43}\text{Al}_{52}\text{Sp}_1\text{Gr}_4\text{An}_0\text{Uv}_0$	1.43	$308(40)T^{-0.955(23)} + 0.00030(1)T$	1350	0.005
Ternary	$\text{Py}_{40}\text{Al}_{49}\text{Sp}_{1.3}\text{Gr}_{10.7}\text{An}_0\text{Uv}_0$	1.23	$136(16)T^{-0.835(21)} + 0.00021(1)T$	1300	0.001
Ant Hill	$\text{Py}_{35}\text{Al}_{43.5}\text{Sp}_{1.7}\text{Gr}_{19.8}\text{An}_0\text{Uv}_0$	1.25	$153(16)T^{-0.856(2)} + 0.00026(1)T$	1300	0.002
Al-Gr ^c	$\text{Py}_5\text{Al}_{72}\text{Sp}_3\text{Gr}_{17}\text{An}_0\text{Uv}_3$	1.04	$85(6)T^{-0.78(1)}$	1150	0.003
Al-Py ^c	$\text{Py}_{21}\text{Al}_{73}\text{Sp}_{1.5}\text{Gr}_{4.5}\text{An}_0\text{Uv}_0$	1.25	$58(11)T^{-0.68(3)}$	1250	0.02
Al-Sp	$\text{Py}_1\text{Al}_{61}\text{Sp}_{37}\text{Gr}_1\text{An}_0\text{Uv}_0$	1.55	$584(64)T^{-1.051(2)} + 0.00027(1)T$	1050	0.001
Spessartine	$\text{Py}_0\text{Al}_3\text{Sp}_{96}\text{Gr}_1\text{An}_0\text{Uv}_0$	1.99	$4080(1700)T^{-1.357(75)} + 0.00039(4)T$	1350	0.036
Sp-rich	$\text{Py}_5\text{Al}_{15.7}\text{Sp}_{61}\text{Gr}_{18.3}\text{An}_0\text{Uv}_0$	1.18	$212(36)T^{-0.923(30)} + 0.00026(1)T$	1350	0.002
Grossular-dry	$\text{Py}_0\text{Al}_{1.3}\text{Sp}_{0.1}\text{Gr}_{95.6}\text{An}_3\text{Uv}_0$	2.79	$2977(500)T^{-1.234(31)} + 0.00037(3)T$	1350	0.024
Grossular-wet	$\text{Py}_0\text{Al}_{1.3}\text{Sp}_{0.1}\text{Gr}_{95.6}\text{An}_3\text{Uv}_0$	2.5	$1583(280)T^{-1.146(30)} + 0.00031(2)T$	1270	0.005
Mn-rich Gr ^{b,d}	$\text{Py}_3\text{Al}_0\text{Sp}_0\text{Gr}_{89.3}\text{An}_{2.4}\text{X}_{5.3}$ ^d	2.86	$629(200)T^{-0.956(55)} + 0.00020(6)T$	1250	0.028
Gr-An 1	$\text{Py}_3\text{Al}_0\text{Sp}_0\text{Gr}_{85.6}\text{An}_{11}\text{Uv}_{0.1}$	2.82	$4579(960)T^{-1.31(4)} + 0.00037(3)T$	1270	0.04
Gr-An 2	$\text{Py}_{0.6}\text{Al}_{1.6}\text{Sp}_{0.4}\text{Gr}_{79.3}\text{An}_{18.1}\text{Uv}_0$	2.77	$1278(270)T^{-1.063(38)} + 0.00037(3)T$	1350	0.02
Andradite	$\text{Py}_{0.1}\text{Al}_0\text{Sp}_{0.3}\text{Gr}_{1.0}\text{An}_{98.4}\text{Uv}_{0.1}$	2.8	$2914(1200)T^{-1.233(73)} + 0.00037(6)T$	1270	0.06
Fo [001] ^e	Mg_2SiO_4	5.15	$12232(1100)T^{-1.371(16)} + 0.00021(2)T$	1350	0.06
Fo:Co [010]	$\text{Mg}_{1.99}\text{Co}_{0.01}\text{SiO}_4$	2.6	$34868(6100)T^{-1.68(3)} + 0.00017(2)T$	1450	0.03
Fo:Co [001]		4.17	$10192(2600)T^{-1.371(46)} + 0.00020(5)T$	1750	0.07
Olivine [100]	$\text{Mg}_{1.84}\text{Fe}_{0.16}\text{SiO}_4$	3.25	$16911(6700)T^{-1.521(70)} + 0.00040(4)T$	1250	0.295
Olivine [010] ^f		1.66	$3642(690)T^{-1.365(33)} + 0.00022(1)T$	1050	0.015
Olivine [001]		2.69	$2467(200)T^{-1.212(16)} + 0.00027(1)T$	1150	0.001
Dunite rock #1	$\text{Mg}_{1.8}\text{Fe}_{0.2}\text{SiO}_4$	2.31	$4013(510)T^{-1.381(22)} + 0.00017(2)T$	1200	0.002
Dunite rock #2	$\text{Mg}_{1.8}\text{Fe}_{0.2}\text{SiO}_4$	2.06	$3276(258)T^{-1.304(14)} + 0.000219(7)T$	1400	0.002
Monticellite rock	$\text{Ca}_{1.15}\text{Mg}_{0.79}\text{Mn}_{0.06}\text{SiO}_4$	1.17	$130(9)T^{-0.837(13)} + 0.000161(7)T$	1200	0.007
Sinhalite [010]	MgAlBO_4 ; 2.1 wt% FeO	5.30	$229260(45000)T^{-1.89(3)} + 0.00038(4)T$	1000	0.04
Chrysoberyl [100]	BeAl_2O_4 ; 0.5 wt% Cr_2O_3	8.99	$92903(9000)T^{-1.63(1)} + 0.00043(3)T$	1270	0.02
Chrysoberyl [010]		6.22	$62270(8500)T^{-1.623(24)} + 0.00030(3)T$	1270	0.013
Chrysoberyl [001]		8.42	$60143(5000)T^{-1.558(15)} + 0.00033(3)T$	1270	0.03
Poly. fayalite	$\text{Fe}_{1.93}\text{Mn}_{0.07}\text{SiO}_4$	1.51	$1628(270)T^{-1.234(29)} + 0.00014(2)T$	1350	0.003
Fayalite rock	$\text{Fe}_{1.84}\text{Mn}_{0.02}\text{Mg}_{0.14}\text{SiO}_4$	1.27	$336(15)T^{-0.986(9)} + 0.00009(5)T$	1200	0.005
Fayalite slag	$\text{Fe}_{1.98}\text{Mn}_{0.02}\text{SiO}_4$	0.80	$151(12)T^{-0.933(14)} + 0.000129(5)T$	1200	0.003
Poly. hortonlite	$\text{Mg}_{1.20}\text{Fe}_{0.80}\text{SiO}_4$	1.47	$250(25)T^{-0.910(2)} + 0.00014(2)T$	1000	0.001
Poly. knebelite	$\text{Fe}_{0.88}\text{Mn}_{0.92}\text{Mg}_{0.20}\text{SiO}_4$	1.245	$242(70)T^{-0.936(50)} + 0.00009(2)T$	1300	0.003
Poly. MnGeO ₄	MnGeO_4	1.24	$2139(636)T^{-1.331(52)} + 0.00020(2)T$	1000	0.035
Yellow opx [100] ^g	$\text{Ca}_{0.01}\text{Mg}_{1.96}\text{Fe}_{0.02}\text{Al}_{0.01}\text{Si}_2\text{O}_6$	2.70	$41022(20000)T^{-1.703(87)} + 0.00031(5)T$	1250	0.077
Yellow opx [010]		1.93	$5612(1700)T^{-1.41(5)} + 0.00016(2)T$	1350	0.017
Clear opx [210]	$\text{Ca}_{0.01}\text{Mg}_{1.93}\text{Fe}_{0.02}\text{Al}_{0.07}\text{Si}_{1.97}\text{O}_6$	2.34	$22498(8700)T^{-1.623(68)} + 0.00037(5)T$	1000	0.010
Green opx [100]	$\text{Ca}_{0.02}\text{Mg}_{1.8}\text{Fe}_{0.15}\text{Cr}_{0.01}\text{Al}_{0.02}\text{Si}_2\text{O}_6$	1.85	$7683(3000)T^{-1.48(7)} + 0.00033(3)T$	1200	0.015
Green opx [010]		1.77	$11843(3000)T^{-1.563(45)} + 0.00032(2)T$	1200	0.006
Green opx [001]		3.10	$16833(9000)T^{-1.53(9)} + 0.00051(6)T$	1350	0.185
Orange opx [100]	$(\text{NaCa})_{0.01}\text{Mg}_{1.77}\text{Fe}_{0.18}\text{Mn}_{0.01}\text{Si}_2\text{O}_6$	1.92	$3308(55)T^{-1.33} + 0.00023(2)T$	1200	0.027 ^h
Orange opx [010]		1.80	$3274(37)T^{-1.33} + 0.00018(1)T$	1350	0.010 ^h
Orange opx [001]		3.30	$14747(280)T^{-1.5} + 0.00047(3)T$	1350	0.11 ^h
Poly. protoenstatite ⊥ c	$\text{Ca}_{0.01}\text{Mg}_{1.95}\text{Al}_{0.04}\text{Si}_{1.98}\text{O}_6$	1.04	$407(129)T^{-1.051(55)} + 0.00004(2)T$	1100	0.001
Diopside-Na [100] ⁱ	$[\text{Na}_{0.03}\text{Ca}_{0.99}](\text{Mg}_{0.94}\text{Fe}_{0.02}\text{Al}_{0.02})\text{Si}_2\text{O}_6$	2.54	$3066(800)T^{-1.253(47)} + 0.00010(3)T$	1100	0.014
Diopside-Na ~[001]		3.83	$1286(180)T^{-1.024(24)} + 0.00021(5)T$	1100	0.017
Diopside-Fe ⊥ c	$\text{Ca}(\text{Mg}_{0.92}\text{Fe}_{0.03}\text{Mn}_{0.01})\text{Si}_2\text{O}_6$	2.32	$1282(230)T^{-1.114(33)} + 0.00004(2)T$	1350	0.026
Diopside-Fe [001]		3.80	$2571(290)T^{-1.148(20)} + 0.00022(2)T$	1550	0.019
Augite [010]	$\text{Ca}(\text{Mg}_{0.77}\text{Fe}_{0.08}\text{Al}_{0.16})(\text{Al}_{0.2}\text{Si}_{1.8})\text{O}_6$	1.55	$428(27)T^{-0.99(1)} + 0.000135(6)T$	1450	0.001
Augite [001]		2.73	$1723(300)T^{-1.146(31)} + 0.00033(2)T$	1450	0.012
Aegirine [110]	$[\text{Na}_{0.88}\text{Ca}_{0.09}\text{Mn}_{0.02}](\text{Fe}_{0.98}\text{Ti}_{0.02})\text{Si}_2\text{O}_6$	1.45	$4408(1900)T^{-1.414(77)} + 0.00023(3)T$	1100	0.068

(Continued)

Table 1 (Continued)

Sample	Simplified formula	D_{298} ($\text{mm}^2 \text{ s}^{-1}$)	$D(T)$	$T_{\text{fit,max}}$ (K)	χ^2
Aegirine [001]		2.76	$1291(230)T^{-1.091(33)} + 0.00036(4)T$	1100	0.019
Poly. jadeite#1	$\text{Na}_{0.98}\text{AlSi}_2\text{O}_6$	2.79	$963(15)T^{-0.716(67)} + 0.00064(6)T$	900	0.001
Poly. jadeite#2	$(\text{Na}_{0.89}\text{Ca}_{0.08})[\text{Mg}_{0.08}\text{Fe}_{0.12}\text{Al}_{0.80}]\text{Si}_2\text{O}_6$	1.84	$453(11)T^{-0.21}$	900	0.01
Spodumene [110] ^f	$\text{LiAl Si}_{1.93}\text{O}_6$ (trace Fe, Mn)	2.19	$2828(670)T^{-1.277(41)} + 0.00025(4)T$	900	0.050
Spodumene [001] ^f		3.66	$4770(1000)T^{-1.276(38)} + 0.00047(5)T$	900	0.004
Low sanidine [100] ^{k,j}	$\text{K}_{0.92}\text{Na}_{0.08}\text{Al}_{0.99}\text{Fe}_{0.01}\text{Si}_{2.95}\text{O}_8$	0.80	$25(3)T^{-0.613(21)} + 0.00014(1)T$	1200	0.0006
Low sanidine [010]		1.34	$52.2(5.8)T^{-0.657(19)} + 0.00027(1)T$	1200	0.001
Low sanidine [001]		1.11	$41.3(4.6)T^{-0.647(20)} + 0.00020(1)T$	1200	0.001
Albite [100] ^m	$\text{K}_{0.01}\text{Na}_{0.98}\text{Al}_{1.01}\text{Si}_3\text{O}_8$	1.08	$284(98)T^{-0.996(61)} + 0.00011(4)T$	1100	0.004
Albite [010]		1.69	$224(27)T^{-0.858(20)} + 0.00021(1)T$	1300	0.001
Albite [001]		1.35	$116(35)T^{-0.784(54)} + 0.00011(4)T$	1100	0.004
FBM [100] ^m	$\text{K}_{0.01}\text{Na}_{0.39}\text{Ca}_{0.59}\text{Al}_{1.61}\text{Fe}_{0.01}\text{Si}_{2.39}\text{O}_8$	0.632	$4.22(75)T^{-0.343(32)} + 0.000085(15)T$	1300	0.0006
FBM [010]		0.794	$5.53(90)T^{-0.351(29)} + 0.00012(2)T$	1300	0.0006
FBM [001]		0.776	$3.37(30)T^{-0.262(16)} + 0.00004(1)T$	1300	0.0002
Synthetic spinel ⁿ	MgAl_2O_4 (initially disordered)	5.28	$4849(850)T^{-1.205(30)} + 0.00026(4)T$	1650	0.18
Gray spinel	$\text{Mg}_{0.96}\text{Fe}_{0.01}\text{Zn}_{0.02}\text{Al}_2\text{O}_4$ (disordered)	5.12	$5595(700)T^{-1.230(10)} + 0.00030(2)T$	1900	0.06
Pink spinel	$\text{MgFe}_{0.004}\text{Cr}_{0.004}\text{Al}_{1.99}\text{O}_4$	7.62	$13206(1000)T^{-1.313(14)} + 0.00018(3)T$	1000	0.02
Blue spinel	$(\text{Mg}_{0.98}\text{Fe}_{0.02})(\text{Fe}_{0.01}\text{Al}_{1.99})\text{O}_4$	4.70	$2231(200)T^{-1.089(14)} + 0.0004(2)T$	1000	0.12
Gahnite	$\text{Zn}_{0.96}\text{Fe}_{0.05}\text{Al}_{1.99}\text{O}_4$	5.94	$3030(330)T^{-1.093(17)} + 0.0004(2)T$	1200	0.09
Hercynite C1	$\text{Mg}_{0.81}\text{Zn}_{0.02}\text{Fe}_{0.28}\text{Al}_{1.89}\text{O}_4$	2.02	$52.7(3.5)T^{-0.571(11)} + 0.0004(2)T$	1400	0.02
Hercynite T	$\text{Mg}_{0.76}\text{Zn}_{0.01}\text{Fe}_{0.37}\text{Al}_{1.84}\text{O}_4$	1.85	$17.4(5)T^{-0.401(5)} + 0.0004(2)T$	1400	0.04
Hercynite M	$\text{Mg}_{0.73}\text{Zn}_{0.02}\text{Fe}_{0.35}\text{Al}_{1.92}\text{O}_4$	1.62	$30.6(1.1)T^{-0.512(6)} + 0.0004(2)T$	1500	0.03
Hercynite U	$\text{Mg}_{0.60}\text{Fe}_{0.65}\text{Al}_{1.73}\text{Ti}_{0.03}\text{O}_4$	1.32	$9.35(23)T^{-0.353(3)} + 0.0004(2)T$	1500	0.013
Perovskite-cubic ^o	$\text{KTaO}_3 + \text{SrTiO}_3 + \text{LaAlO}_3$	4.5	$2448(500)T^{-1.11(4)} + 0.00020(5)T$	1600	0.3
Perovskite-1 [100]	YAlO_3	3.76	$21555(6000)T^{-1.52(5)} + 0.00022(3)T$	1800	0.08
Perovskite-2 [001]	$\text{YAlO}_3\text{:Tm}$	2.91	$5261(800)T^{-1.326(27)} + 0.00026(2)T$	1300	0.006
Perovskite-3 [100]	NdGaO_3	1.93	$1743(250)T^{-1.205(25)} + 0.00018(1)T$	1500	0.003
Perovskite-3 [010]	NdGaO_3	1.84	$3158(600)T^{-1.316(34)} + 0.00023(2)T$	1500	0.005
Perovskite-3 [001]	NdGaO_3	2.02	$1894(200)T^{-1.208(2)} + 0.00016(1)T$	1500	0.005
Corundum [1120] ^p	Al_2O_3	11.1	$5.7169(2.8) \times 10^5 T^{-1.915(87)} + 0.0007(1)T$	1500	0.44
Corundum [0001]	Al_2O_3	12.0	$4.9238(2.1) \times 10^5 T^{-1.875(74)} + 0.0006(1)T$	1500	0.44
Ceramic corundum	Al_2O_3 (~0% porosity)	12.0	$2.06(40) \times 10^5 T^{-1.72(3)} + 0.00040(4)T$	1900	0.67
Hematite [1100]	Fe_2O_3	1.90	$5947(2800)T^{-1.424(82)} + 0.00029(3)T$	1200	0.02
Hematite [0001]	Fe_2O_3	2.80	$10107(3400)T^{-1.443(58)} + 0.00020(3)T$	1200	0.02
Poly. ilmenite [0001]	FeTiO_3	0.96	$11.465(1.0)T^{-0.437(20)} + 0.00055(2)T$	1150	0.004
Quartz [100] ^r	SiO_2	3.73	$2.585(733) \times 10^5 T^{-1.971(49)} + 0.00055(4)T$	1300	0.014
Quartz [001]	SiO_2	7.00	$1.017(200) \times 10^6 T^{-2.089(46)} + 0.00067(4)T$	1300	0.036
Poly. cristobalite ^q	SiO_2	1.85	$392370(21400)T^{-2.177(95)} + 0.00053(2)T$	1250	0.009
Fused quartz glass ^s	SiO_2 (36 ppm H_2O)	0.85	$7.96(97)T^{-0.409(21)} + 0.00022(1)T$	1700	0.0006
Rutile (syn) [110] ^t	TiO_2	1.40	$49.31(12.4)T^{-0.632(44)} + 0.00011(3)T$	1700	0.001
Rutile (syn) [001]	TiO_2	2.56	$85.83(8.2)T^{-0.616(17)} + 0.00004(2)T$	1700	0.002
Rutile natural [001]	$\sim\text{TiO}_2$	1.97	$109.3(13.6)T^{-0.705(2)} + 0.000084(17)T$	1700	0.001
Periclase ^u	MgO	15.22	$35764(2200)T^{-1.364(11)} + 0.000084(17)T$	1650	0.2
Ceramic periclase	MgO (2–4% porosity)	13.72	$16282(960)T^{-1.249(10)} + 0.000084(17)T$	2100	0.26
B1 = rock salt	LiF	3.46	$24502(4400)T^{-1.565(30)} + 0.000084(17)T$	1100	0.05
Halite	NaCl #2	3.48	$45404(3000)T^{-1.669(11)} + 0.000084(17)T$	1100	0.005
NaI	NaI	1.17	$6518(750)T^{-1.523(19)} + 0.000084(17)T$	670	0.0007
NaI:TI	NaI:TI	0.9	$5637(600)T^{-1.527(19)} + 0.000084(17)T$	670	0.0007
Sylvite	KCl #2	5.15	$311550(34000)T^{-1.938(18)} + 0.000084(17)T$	900	0.02

(Continued)

Table 1 (Continued)

Sample	Simplified formula	D_{298} ($\text{mm}^2 \text{ s}^{-1}$)	$D(T)$	$T_{fit,max}$ (K)	χ^2
KBr	KBr	2.26	$37\,743(4000)T^{-1.711(13)}$	800	0.002
B2	CSl:Ti	0.96	$9123(1000)T^{-1.613(19)}$	650	0.0004
Graphite AXM ^v	C	70	$26\,290(3300)T^{-1.035(22)} + 0.00064(17)T$	2600	0.80
Graphite ZXF ^w	C	50	$16\,219(2000)T^{-1.02(2)} + 0.00067$	1300	2.0
Glassy carbon ^x	C	6.20	$74.84(2.35)T^{-0.447(5)} + 0.00079(2)T$	2600	0.80

Notes: T_{max} is the limit to which all these fits can be projected to. All fits used starting parameters of $c1 = 100$, $c2 = 1$, and $c3 = 0.001$. Poly = polycrystalline.

^aGarnet data from Hofmeister (2006). The formulas for natural samples are provided in terms of end-members: Py = pyrope = $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$; Al = almandine = $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$;

Sp = spessartine = $\text{Mn}_3\text{Al}_2\text{Si}_3\text{O}_{12}$; Gr = grossular = $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$; An = andradite = $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$ where the iron is ferric; Uv = uvarovite = $\text{Ca}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$.

^bSmall sample with uncertainties greater than 2%.

^cFractured during the run, adding uncertainties.

^dUnusual composition: X = $\text{Ca}_3\text{Mn}_2\text{Si}_4\text{O}_{12}$.

^eOlivine data from Pertermann and Hofmeister (2006).

^fIdentical values obtained from olivine from Sumput [010] with similar Fe content ($\text{Mg}_{1.87}\text{Fe}_{0.13}\text{SiO}_4$).

^gOrthopyroxene and protoenstatite data from Hofmeister (2012). G was fixed for orange orthopyroxene.

^hFor these cases, the fit was inadequate at high T . Fits reported are for fixing g near the value obtained for an unconstrained fit.

ⁱClinopyroxene data from Hofmeister and Pertermann (2008).

^jTwo similar samples gave identical fits.

^kFeldspar data from Pertermann et al. (2008), Hofmeister et al. (2009), and Branlund and Hofmeister (2012).

^lThe direction perpendicular to [010] and [001].

^mThese orientations are the face orthogonal to (001) and (010).

ⁿSpinel data from Hofmeister (2007c).

^oPerovskite data from Hofmeister (2010a).

^pHofmeister (2014). For [1120] of corundum, the data are better described by $D(T) = 1400(65)T^{-1} + 158(7) \times 10^6 T^{-3} + 0.00030(7)T$ with $\chi^2 = 0.12$, and for [001], the data are better described by $D(T) = 1580(60)T^{-1} + 167(6) \times 10^6 T^{-3} + 0.00015(7)T$ with $\chi^2 = 0.11$. For ceramic corundum, a better fit is $D(T) = 824(95)T^{-1} + 7.75(30) \times 10^5 T^{-3} + 0.00028(5)T$ with $\chi^2 = 0.52$.

^qHofmeister (2013).

^rBranlund and Hofmeister (2007).

^sHofmeister and Whittington (2012).

^tHofmeister (2005).

^uB1 and B2 data from Yu and Hofmeister (2011).

^vHigh-temperature data from Clark and Taylor (1975) and Baba and Cezairliyan (1994).

^wBlumm and Lemarchand (2002). H is not well constrained so fits were made by setting this to $0.006 \text{ mm}^2 \text{ s}^{-1} \text{ K}^{-1}$ as observer for the other graphite sample.

^xBaba and Ohno (2001).

The observed temperature dependence for D shows that phonon scattering coexists with a second mechanism for conduction of lattice vibrational energy, the sum of which produces the observed thermal diffusivity or conductivity. Whereas the $c_1 T^{-c_2}$ term is consistent with phonon scattering, the contrasting behavior described by the $c_3 T$ term is consistent with some type of diffusive radiative transfer, such as radiative transfer of IR polaritons ($D_{\text{IR,tad}}$) proposed by Hofmeister et al. (2014). Both terms represent heat transport at slow (and similar) speeds, since ballistic radiative transfer of light at fast speeds (c/n) is removed during processing of the raw data (the time–temperature curves; Mehling et al., 1998).

2.23.4.2 Monophase Crystalline Aggregates: Comparison to Isochemical Crystals

Crystalline aggregates of a few geologically important materials (fayalite, dunite, protoenstatite, quartzite, cristobalite, and ceramic periclase and corundum) are included in Table 1 and/or Figures 12 and 13. Porosity has a large effect, as shown by LFA data on quartzites and microcrystalline SiO_2

samples (Branlund and Hofmeister, 2008). However, the SiO_2 solids also have variations in grain size, order/disorder, and material filling the pores (water, air, and/or secondary phases), which made precisely quantifying effects of these three parameters difficult. Data on ceramic corundum and periclase (Hofmeister, 2014b; Hofmeister and Yuen, 2007) help clarify the effects.

Nonporous ceramic Al_2O_3 has D within uncertainty of the slightly faster orientation (Figure 12(c) and 12(d)). The sample's grain size (mean size of $10 \mu\text{m}$) is not small enough to reduce thermal transport. Similarly, pressed pellets of alkali halides that are optically clear (i.e., pores containing water and air were removed) have nearly the same $D(T)$ as chemically equivalent single crystals (Yu and Hofmeister, 2011). Inference of grain size impeding heat transport from contact measurements (Smith et al., 2003) seems to be connected with both very small ($1 \mu\text{m}$) grain size from their formula and porosity (also see discussion by Branlund and Hofmeister, 2008).

Porous ceramic MgO has lower D than the single crystal. High-temperature data on another ceramic sample are similar, perhaps with a slightly higher D . The very high- T data have

larger uncertainties (Figure 12(d)) because coatings gradually reacted with trace water or O₂ gas in the purge, making ballistic radiative transfer large and difficult to model accurately.

Monomineralic rocks have considerably larger grains (~100 μm) than ceramic and may have larger pores, as well as a wider distribution of grain and pore sizes. The dunite aggregates have D between that of the oriented single crystals, whereas quartzite has D similar to the orientation with lower D , and fine-grained agate has higher D than coarse-grained quartzite and behaves more like quartz (Figure 13). These differences are attributed to differential expansion of large grains during heating, which can create pore space and microcracks.

Although more measurements of samples with known porosity and grain size are needed to isolate and quantify this effect, it appears that D of natural samples that are fine-grained

and not porous should equal orientationally averaged single-crystal data. Importantly, our measurements involve free-standing samples. In the Earth, confining pressure would minimize the effects of porosity, permitting representation of interior conditions with single-crystal data.

2.23.4.3 Effect of Impurities on Room-Temperature Values

That impurity ions lower D and k_{lat} is well known (e.g., Slack, 1964). The type of ion appears to be unimportant (e.g., OH⁻ for O²⁻ or Fe for Mg). For solid solutions, the lowest values of D or k_{lat} are measured near the middle of each binary, with steep decreases from end-member values, as shown for pyroxenes (Figure 14). Spinel behaves similarly (Hofmeister, 2007c).

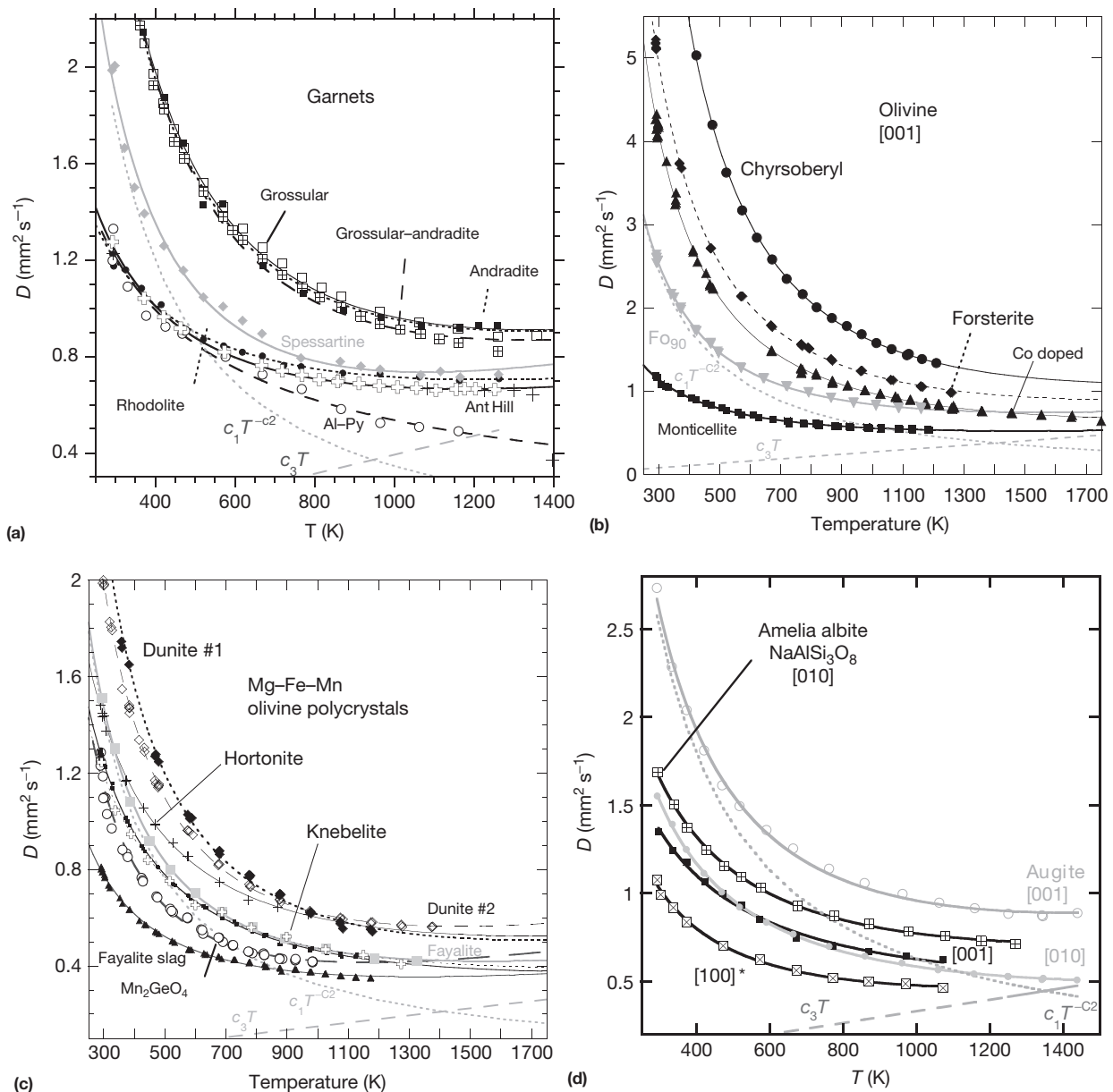


Figure 12 (Continued)

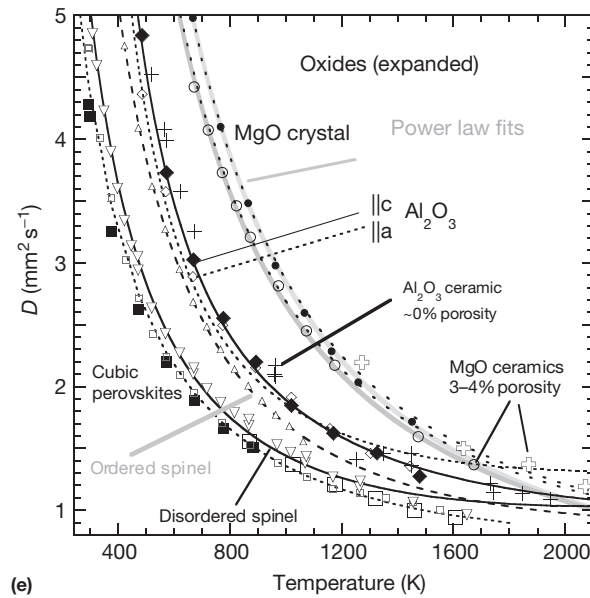


Figure 12 Laser flash (at 1 atm) showing D as a function of temperature. Symbols = average of three data points at a given temperature. Unless specified, the curves = fits of Table 1, which also provides data sources. In each panel, the components of the fit are shown for one sample. Gray dotted curve = phonon component. Gray dashed curve = IR photon component. (a) Garnet single crystals. Gray diamonds = new data on near end-member spessartine sample. (b) Olivine single crystals with heat flow $\parallel c$ plus a rock of mostly MgCaSiO_4 . This orientation provides the average values of D . (c) Polycrystals and rocks of various olivine compounds. Gray = new data on fayalite from Rockport, MA, with $\text{Fe}_{1.93}\text{Mn}_{0.07}\text{SiO}_4$ and negligible Mg. Open plus = new data on knebelite from Dannemora, Sweden, with $\text{Fe}_{0.89}\text{Mn}_{0.92}\text{Mg}_{0.20}\text{SiO}_4$. Tiny squares = mostly fayalite rock from Buffalo, NY. (d) Albite (squares and black lines) from Hofmeister et al. (2009); augite (circles and gray lines) from Hofmeister and Pertermann (2008). (e) Expanded view of oxides and commercial ceramics. Gray curves = power law fits. Two different sections of MgO ceramic were studied. Another MgO ceramic from a different manufacturer provided even lower D values (not shown). The power law fits for ceramic MgO do not accurately depict the flat trends above 1600 K. All three cubic perovskites studied define a single trend. Black squares = SrTiO_3 . Large squares = LaAlO_3 . Small squares = KTaO_3 .

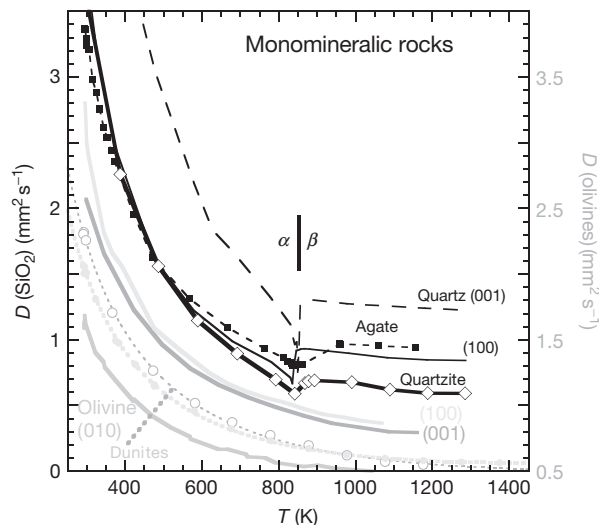


Figure 13 Comparison of essentially monomineralic rocks to oriented single crystals of olivine and quartz. Fits in Table 1 exclude effects of the displacive transition in SiO_2 near 850 K. Solid gray = the three orientations of orthorhombic olivine. Coarse-grained dunites and quartzite are similar to the average D at low temperature but decrease more rapidly at high T , likely due to cracks forming during differential expansion. Cryptocrystalline agate remains near the average at all temperatures.

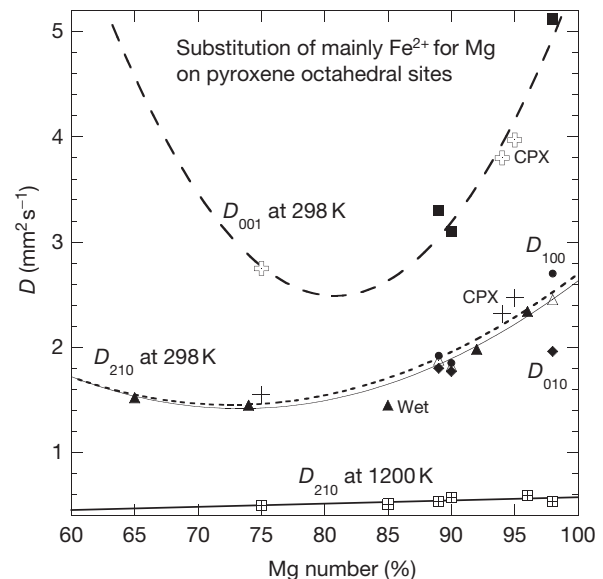


Figure 14 Effect of cation disorder on thermal diffusivity of pyroxenes. Orthopyroxene is the only silicate mineral where the effect of Fe content has been quantified using LFA but this is only at 0–45% Fe content. Measurements were made with heat flow perpendicular (D_{210} , dashed line and triangles; D_{101} , solid line and circles) and parallel (D_{001} , long dashed lines and squares) to c . Values for clinopyroxenes, plus signs, are similar. Reproduced from Hofmeister AM (2012) Thermal diffusivity of orthopyroxenes at elevated temperature. *European Journal of Mineralogy* 24: 669–681.

2.23.5 Thermal Diffusivity of Magnesium Silicate Perovskite at Temperature and Pressure

Laser-flash data have been collected on perovskites other than (Mg,Fe)SiO₃ as these samples are too small for LFA and because of reversion of uncompressed material at low temperatures. Orthorhombic NdGaO₃ should best represent MgSiO₃ perovskite, based on the behavior of garnets of similar compositions, and cubic oxide perovskites follow one trend for D versus T (Figure 12(d)). This inference is corroborated by contact measurements of $D = 1.72 \text{ mm}^2 \text{ s}^{-1}$ for silicate perovskite, which should be 10% lower than the bulk D and also fall 10% lower than the average of D for the three orientations of NdGaO₃ (Figure 15).

In the contact measurements of Manthilake et al. (2011), spurious radiative transfer is evidenced by the weaker temperature dependence than LFA results on periclase and perovskites. Spurious radiative transfer cannot be removed from contact measurements by data processing. Periclase, including iron-bearing, is more transparent in the mid-IR than perovskite and should have more radiative transfer. However, their D values at pressure are clearly too low compared to ambient LFA data on MgO (Figure 15). Apparently substantial contact losses occur for periclase samples. Because the technique involves a wire run through a hole in the sample, the degree of loss is specific to each experimental run.

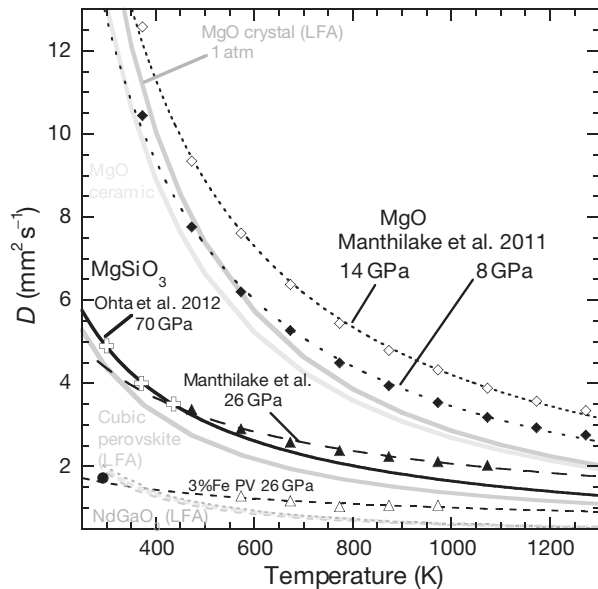


Figure 15 Comparison of the temperature dependence from high-pressure experiments (black curves and symbols) to LFA results (gray curves, as labeled). The Ångström contact method was used by Osako and Ito (1991) at 1 atm (large dot) and by Manthilake et al. (2011) in a multianvil device (triangles or diamonds and broken lines). The trend for MgO of $D/D_{298} = T^{-1.08}$ being shallower than LFA, as is common in all contact experiments, is due to spurious radiative transfer. Thermoreflectance (plus signs and solid line) for MgSiO₃ in a DAC by Ohta et al. (2012) gives $D/D_{298} = T^{-0.90}$, which is similar to LFA of perovskite compounds, which corroborates that Manthilake et al.'s results are affected by radiative transfer.

The temperature dependence of D for MgSiO₃ from thermoreflectance (Ohta et al., 2012) has a trend similar to LFA data at low temperature (Figure 15; Table 1). Over the temperature range explored, spurious radiative transfer would not change significantly. This result shows that spurious radiative transfer is small in the measurements of Ohta et al. (2012).

The P dependence of D from Ohta et al. (2012) extrapolates to 30% higher than Osako and Ito's (1991) contact measurement and provides a rate similar to that predicted from eqn [11] (Figure 16). Given the uncertainties in the data, and especially the increasing uncertainty in D and P with pressure, thermoreflectance data on silicate perovskite agree with the quasiharmonic phonon-gas model using measured values of thermodynamic properties. In addition, Ohta et al. (2012) showed that the transition to the postperovskite phase causes D to almost double, which was predicted by Hofmeister (2007b) using the DHO model.

The fits of thermoreflectance data to T and P in Figures 15 and 16 are consistent with LFA measurements and models of phonon scattering. Comparison with measurements outside the DAC indicates that the thermoreflectance data of Ohta et al. (2012) are systematically 10% too high, due to small amounts of radiative transfer. Otherwise, contact losses in Osako and Ito (1991) must be ~30%, which is comparatively large (Figure 8), but possible.

Contact measurements of Manthilake et al. (2011) do not provide accurate D values for perovskite or periclase or their P and T derivatives, based on comparison with models and independent measurements.

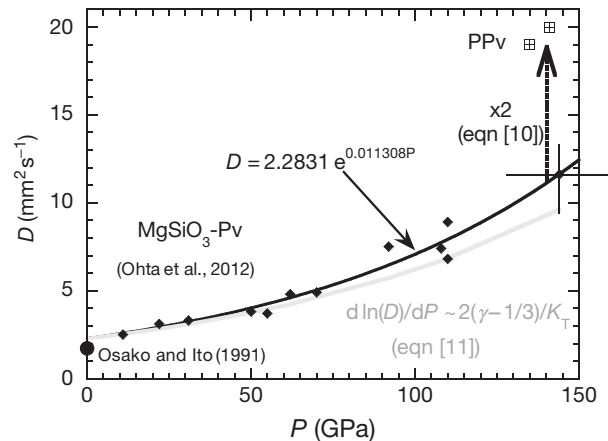


Figure 16 Comparison of thermoreflectance for MgSiO₃ in a DAC by Ohta et al. (2012) to DHO-phonon gas model. Due to the change in contents of the primitive unit cell, D of postperovskite should be double that of perovskite, presuming lifetimes and speeds do not change significantly. The curve fit to the data (diamonds) weighs each point equally, which overemphasizes the more uncertain (thin lines) high- P data points. Higher D at 1 atm of the fit is consistent with the contact measurement of Osako and Ito (1991) being low by 10–20% due to contact losses. This sample was polycrystalline and should not have significant radiative transfer at 300 K.

2.23.6 Lattice Thermal Conductivity and Its Temperature Dependence

To first order, Earth's slow heat transfer is described by eqn [3] and LFA of D . Thermal conductivities of electrically insulating crystals peak near room temperature due to contrasting T dependence of three physical properties in eqn [3]. At 298 K and above, k mostly decreases, as exemplified in Figure 17. Using the parameterization for C_p provided by Berman and Brown (1985) and that density depends very weakly on temperature leads to the high- T equations

$$k = \left(a' + \frac{b'}{T} + c'T \right) \left(d' + \frac{e'}{T^{1/2}} + \frac{f'}{T} + \frac{g'}{T^2} \right) \quad [35]$$

$$= a'' + b''T + c''T^{1/2} + \frac{d''}{T^{1/2}} + \frac{e''}{T} + \frac{f''}{T^{3/2}} + \dots$$

In fitting mineral data, we found that most phases can be fit by the simple form

$$k = \left(a + \frac{b}{T} + cT \right) \quad [36]$$

The linear term in k exists due not only to the form for $D(T)$ but also to the anharmonic correction to heat capacity: $C_p = C_v(1 + \alpha\gamma_{th}T)$. Because α and γ_{th} weakly depend on T and C_v is constant at high T for a perfectly harmonic solid, the high- T behavior of k must contain a linear contribution.

Thermal conductivities of mafic minerals all cluster together (Figure 18(a)). For felsic rocks, their high proportions of feldspars create lower k values and a bigger spread in k compared to ultramafic rocks (Figure 18(b)). Importantly, thermal conductivity of olivine and enstatite are very close to our composite value for the oceanic lithosphere and upper mantle.

2.23.7 Conclusions

Methods most commonly used to measure k or D in geologic science involve contacts and fall short of providing accurate measurements of phonon transport, due to the presence of both unwanted ballistic radiative transfer and resistance at contact interfaces. The laser-flash technique is accurate, benchmarked against soft, opaque materials, but one drawback is that the sample size required is too large for high-pressure synthetics, and another is the cost of the instrumentation. Improving accuracy and precision in determining heat transport properties requires further application of existing all-optical techniques to a greater variety of minerals and high-pressure structures and, possibly, development of additional all-optical techniques with similar or greater accuracy than the laser-flash measurements. The PTGS method is not recommended, as the results reflect processes in addition to thermal relaxation. Thermoreflectance in the DAC has great promise, but benchmarking is needed against a substance that is opaque in the near-IR, such as metal or graphite.

Available data indicate that the P and T components of D (or of k_{lat}) can be modeled separately and recombined to provide data at mantle conditions. It is fortunate that pressure derivatives for both microscopic processes of phonon scattering and IR radiative transfer are similar, a consequence of quasiharmonic behavior.

Diffusive radiative transport at high frequency was revisited for several reasons. The equations used presently contain a substantive error (n^2 should be deleted) and most treatments neglect grain size. It is fortunate that this phenomenon is mainly a transient phenomenon, so that laboratory measurements, which are far more accurate and definitive, to the first order describe slow cooling of the Earth.

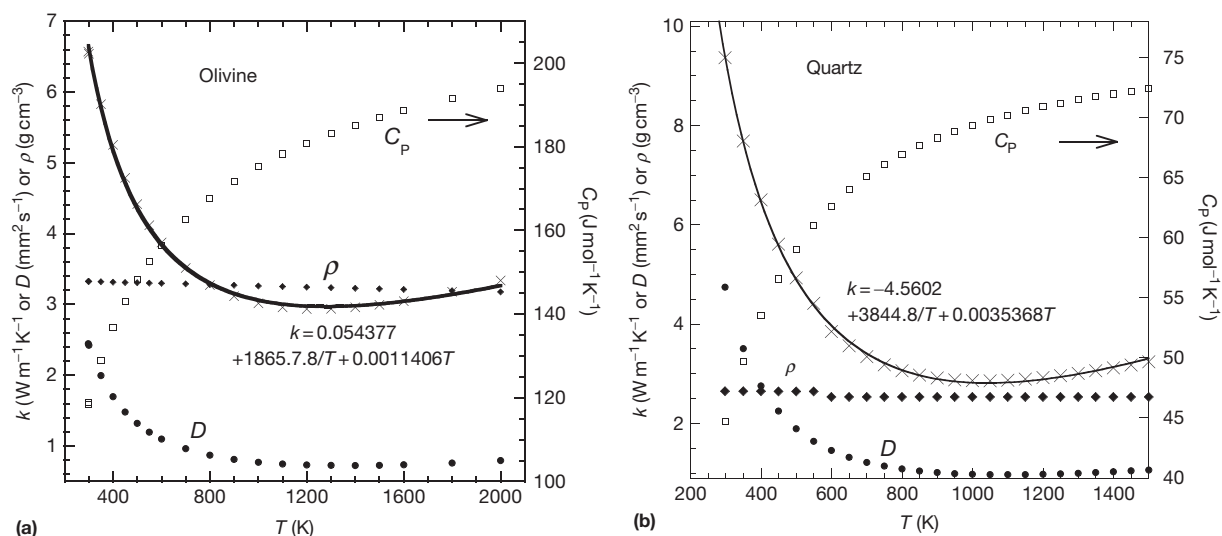


Figure 17 Calculation of bulk values of thermal conductivity (solid curve) from eqn [3]. Symbols = bulk or directionally averaged constituent properties: density (computed using α from Fei, 1995), heat capacity (from Berman and Brown, 1985), and thermal diffusivity (from Table 1). (a) Olivine. (b) Quartz. For both minerals, fits to thermal conductivity are simple despite complicated behavior of the individual comprising physical properties.

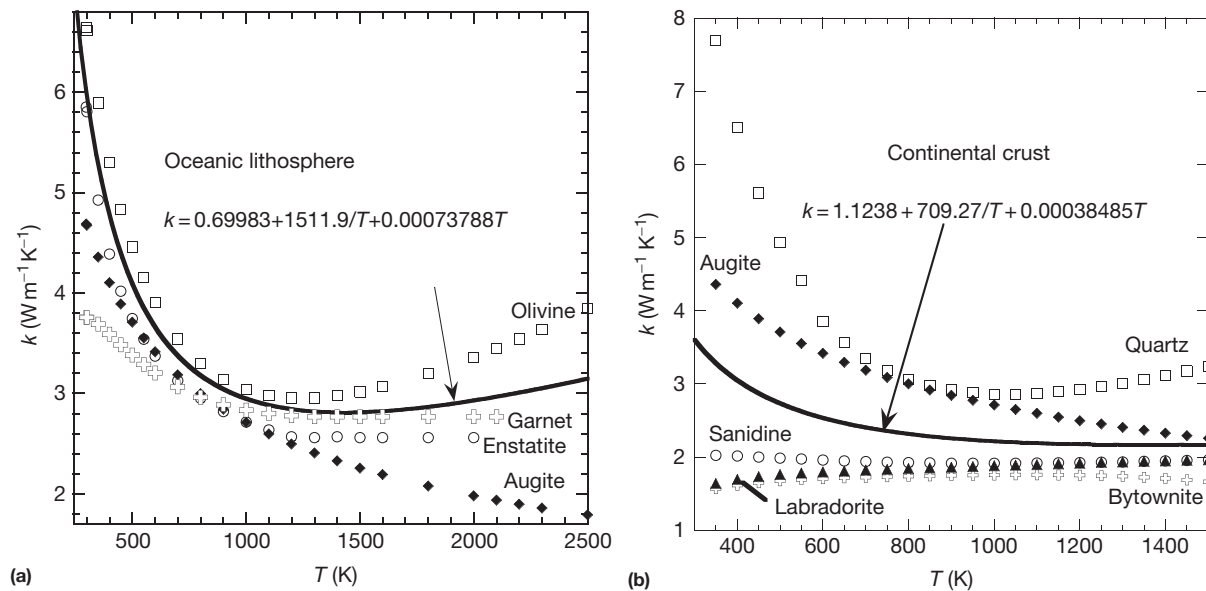


Figure 18 Thermal conductivity of Earth materials as a function of temperature. (a) Oceanic lithosphere and upper mantle=60% olivine + 15% orthopyroxene + 15% clinopyroxene + 10% garnet. (b) Continental crust=20% labradorite + 20% bytownite + 25% augite + 20% low sanidine + 15% quartz. Dots= mineral composites, with the fit shown as a solid line. Various symbols= minerals as labeled, calculated as in Figure 17.

Acknowledgments

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2.24 Magnetic Properties of Rocks and Minerals

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2.24.1 Introduction

Magnetic minerals are pervasive in the natural environment and are present in all types of rocks, meteorites, sediments, and soils. These minerals retain a memory of the geomagnetic field that was present during the rock's formation. Paleomagnetic recordings have been exploited for more than 50 years to map the movements of the continental and oceanic plates on Earth and have also proved to be a powerful tool for reconstructing the geologic history of other planets, moons, and asteroids (Acuna et al., 1999; Connemey et al., 1999, 2004; Fu et al., 2012; Lawrence et al., 2008; Shea et al., 2012; Tarduno et al., 2012). The variation in intensity of the geomagnetic field, as determined from rocks and archaeological material, has been used to provide an understanding of the behavior of the geodynamo and to constrain models of fluid motion in the Earth's core going back over 3.4 billion years (Gallet et al., 2005; Granot et al., 2012; Labrosse and Macouin, 2003; Tarduno et al., 2010; Valet et al., 2005). More recently, magnetism has been used to trace changes in climate, as the concentration and size of magnetic particles incorporated into sediments are highly sensitive to environmental factors (Evans and Heller, 2003). The importance of magnetic archives of paleoclimate has been highlighted by Maher (2008) and Maher and Thompson (2012), who demonstrated that magnetic proxies offer a radically different interpretation of how the Asian monsoon has changed throughout the Holocene than that obtained using geochemical methods.

Interpretations of rock magnetic measurements are completely reliant on an accurate understanding of the physical processes by which a material acquires and maintains a faithful record of the geomagnetic field. Since the pioneering work of Néel (1948, 1949), rock magnetists have attempted to develop a quantitative understanding of how assemblages of magnetic minerals in single-domain (SD), pseudo-single domain (PSD), or multidomain (MD) states acquire and maintain natural remanent magnetization (NRM) (see Dunlop and Özdemir, 1997 for a detailed overview). The theories work well in ideal cases, that is, when magnetic grains are homogeneous, defect-free, and sufficiently well separated from each other that magnetic interactions between them can be neglected. They begin to fail, however, when the mineral is heterogeneous at the nanometer scale, as is necessarily the case when the magnetic grains form part of a nanoscale intergrowth. Recent studies have demonstrated that nanoscale microstructures are extremely common in magnetic minerals and that they have a significant impact on their macroscopic magnetic properties (Brownlee et al., 2010, 2011; Feinberg et al., 2004, 2005; Harrison and Becker, 2001; Harrison et al., 2002, 2005; Kasama et al., 2010; McEnroe et al., 2001, 2002; Robinson et al., 2002, 2004, 2006). These microstructures not only determine the intensity and stability of macroscopic magnetism recorded in rocks – thereby controlling the fidelity of paleomagnetic recordings at the global scale – but also are often important in an industrial context, providing natural analogs of magnetic phenomena (such as exchange bias) that are central to the design of new magnetic recording materials (Fabian et al., 2008; McEnroe et al., 2007; Puentes et al., 2004; Skumryev et al., 2003).

This chapter describes the current state of the art in the field of computational and experimental mineral physics, as applied

to the study of magnetic minerals. Particular emphasis is placed on the relationship between nanoscale microstructure and macroscopic magnetic properties. For a comprehensive review of the magnetic properties of specific rocks and minerals, the reader is referred to Hunt et al. (1995) and Dunlop and Özdemir (1997). Arguably, the most significant recent advance is the application to mineral magnetism of off-axis electron holography, a transmission electron microscopy (TEM) technique that yields a two-dimensional (2-D) vector map of magnetic induction with nanometer spatial resolution (Harrison et al., 2002). Electron holography is capable of imaging the magnetization states of individual magnetic particles and the magnetostatic interaction fields between neighboring particles: two factors that play a central role in the interplay between magnetism and microstructure. By combining this capability with electron tomography, it is now possible to determine both the micromagnetic structures and the 3-D morphologies of nanoscale magnetic particles directly and quantitatively as a function of temperature and applied magnetic field. In tandem with these techniques, advances in the application of atomistic and micromagnetic simulations to the study of magnetic ordering in minerals have opened the way to novel interpretations and modeling of nanoscale magnetic properties (Robinson et al., 2002). Only now are the sizes of systems that are accessible to simultaneous experimental and computational study converging at the nanometer length scale (Bryson et al., 2012). This convergence provides unique opportunities for tackling problems that lie at the frontiers of rock magnetism.

This chapter is organized in order of increasing length scale of magnetic interactions. Section 2.24.2 deals with magnetism at the atomic length scale. It contains a brief description of exchange interactions and magnetic structure in Fe-bearing oxides and the use of atomistic simulations of magnetic ordering to the study magnetism at surfaces and interfaces. Section 2.24.3 deals with magnetism at the nanometer length scale. Following a summary of the theory of electron holography, recent applications of holography to the study of magnetic minerals are reviewed. Section 2.24.4 deals with magnetism at the micrometer length scale, including advances in micromagnetic simulations that allow the magnetic behavior of particles with realistic 3-D morphologies to be modeled. In Section 2.24.5, we move to the macroscopic length scale, with a description of how new approaches for the measurement of macroscopic magnetic properties (i.e., first-order reversal curve (FORC) diagrams) are providing quantitative information about the spectrum of coercivities and interaction fields that exist at the microscopic scale.

2.24.2 Magnetism at the Atomic Length Scale

2.24.2.1 Exchange Interactions and Magnetic Structure in Fe-Bearing Oxides

The driving force for magnetic ordering in Fe-bearing oxides is the superexchange interaction between neighboring transition metal cations via intermediate oxygen anions (Goodenough, 1966). The magnitudes and signs of superexchange interactions define the magnetic ground state and the magnetic ordering temperature of the mineral and play a fundamental

role in determining its macroscopic magnetic properties. The exchange interaction energy for classical spins can be expressed in the form

$$E_{\text{mag}} = - \sum_{i \neq j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \quad [1]$$

where $\mathbf{S}_i$ and $\mathbf{S}_j$ are the spins on atoms i and j and J_{ij} is the corresponding exchange integral. Positive values of J_{ij} lead to parallel (i.e., ferromagnetic) alignment of spins; negative values lead to antiparallel (i.e., antiferromagnetic, AF) alignment.

Empirical values of J_{ij} can be obtained from spin-wave dispersion curves measured using inelastic neutron scattering (Brockhouse, 1957; Glasser and Milford, 1963; Phillips and Rosenberg, 1966; Samuelsen, 1969; Samuelsen and Shirane, 1970; Watanabe and Brockhouse, 1962). Alternatively, theoretical values can be obtained from first-principles calculations (Matar, 2003; Pinney et al., 2009; Sadat Nabi et al., 2010; Sandratskii, 1998). The simplest theoretical approach involves calculating the total energies of several different collinear arrangements of spins and then determining values of J_{ij} directly from eqn [1] (Rollmann et al., 2004; Sandratskii et al., 1996). This approach is limited, however, by the small number of alternative structures that can be generated for a given unit cell. The use of noncollinear magnetic structures (Sandratskii, 1998) provides a more general procedure for calculating exchange integrals out to arbitrary cation–cation separations (Uhl and Siberchico, 1995). This approach is based on the calculation of the total energies of spin-spiral configurations, over a grid of wave vectors within the Brillouin

zone. It is often found that exchange interactions that are determined by spin-wave and first-principles methods overestimate magnetic ordering temperatures significantly (Sandratskii et al., 1996; Uhl and Siberchico, 1995). If necessary, the calculated values of J_{ij} can be scaled or refined to provide better agreement with experimental observations (Burton, 1985; Harrison, 2006; Harrison and Becker, 2001).

Exchange integrals for hematite (Fe_2O_3), ilmenite (FeTiO_3), and magnetite (Fe_3O_4) are listed in Table 1 and Figure 1 (see also Sadat Nabi et al., 2010 for density functional theory-calculated values for Fe_2O_3 , FeTiO_3 , and the Fe_2O_3 – FeTiO_3 solid solution). The crystal structures of hematite–ilmenite and magnetite are compared in Figure 2. Superexchange interactions are highly sensitive to the relative positions of the two cations and the intermediate oxygen anion, varying in magnitude approximately as $\cos^2 \psi$, where ψ is the cation–oxygen–cation bond angle (Coe and Ghose, 1987). In hematite (Figure 2(a)), Fe^{3+} cations occupy two-thirds of the octahedral interstices within a hexagonal close-packed oxygen sublattice, forming symmetrically equivalent A and B layers parallel to the (001) basal plane (space group $R\bar{3}c$). Each octahedron shares a face with an octahedron in the layer above or below and edges with three octahedra in its own layer. Since both face- and edge-sharing octahedral–octahedral linkages have $\psi \sim 90^\circ$ (Table 1), both first- and second-nearest-neighbor interactions are weak. Third- and fourth-nearest-neighbor interactions involve corner-sharing octahedra in adjacent layers ($\psi \sim 120^\circ$ and 132° , respectively; Table 1). These interactions are large and negative, leading to an AF ground state in which A-layer spins are antiparallel to B-layer spins. Above 260 K (the Morin

Table 1 Summary of magnetic exchange integrals for hematite, ilmenite, and magnetite

Nearest neighbor	Cation–cation distance (Å)	Interaction type	Polyhedral sharing	Cation–oxygen–cation bond angle ($^\circ$)	Magnetic interaction parameter (K)
<i>Hematite (spin waves; Samuelsen and Shirane, 1970)</i>					
1	2.9	Interlayer	Face	86.5	12
2	2.971	Intralayer	Edge	93.9	3.2
3	3.36	Interlayer	Corner	119.7	–59.4
4	3.71	Interlayer	Corner	131.6	–46.4
5	3.99	Double	None	N.A.	–2
<i>Ilmenite (spin waves; Ishikawa et al., 1985)</i>					
1	3.03	Intralayer	Edge	89.1	9.8
2	4.074*	Double	None	N.A.	–8.9
3	5.088	Intralayer	None	N.A.	0.56
4	5.9	Intralayer	None	N.A.	0.68
<i>Magnetite (first-principles calculations; Uhl and Siberchico, 1995)</i>					
1	2.97	Oct–Oct	Edge	87.8	9.6
2	3.48	Tet–Oct	Corner	126.8	–33.4
3	3.635	Tet–Tet	None	N.A.	–2.1
4	5.14	Oct–Oct	None	N.A.	–0.17
5	5.45	Tet–Oct	None	N.A.	0.65
6	5.45	Tet–Oct	None	N.A.	0.3
7	5.936	Tet–Tet	None	N.A.	–0.73
8	6.63	Oct–Oct	None	N.A.	–0.48
9	6.88	Tet–Oct	None	N.A.	0.57
10	6.96	Tet–Tet	None	N.A.	0.67
11	7.852	Oct–Oct	None	N.A.	0.13
12	8.06	Tet–Oct	None	N.A.	–0.26
13	8.06	Tet–Oct	None	N.A.	0.2

*Includes contributions from the three nearest double layer interactions.

transition), spins lie parallel to the (001) basal plane and point nearly perpendicular to a $\langle 100 \rangle$ crystallographic axis of the hexagonal unit cell (Tanner et al., 1988). The AF sublattices are canted by an angle of $\sim 0.065^\circ$, leading to a weak parasitic moment lying within the basal plane and directed along $\langle 100 \rangle$ (Dzyaloshinskii, 1958). The choice of six possible $\langle 100 \rangle$ directions for the canted moment leads to a complex magnetic and crystallographic domain microstructure in hematite (Tanner et al., 1988), although its presence has often been overlooked in magnetic studies. By considering arbitrary, noncollinear configurations of the atomic magnetic moments, Sandratskii and Kübler (1996) used first-principles calculations to demonstrate that the canted magnetic structure appears as a direct consequence of spin-orbit coupling (Figure 3). Below the Morin transition, the spin alignment switches to $[001]$, and the canting is lost. A small residual of the weak parasitic moment is often observed in the basal plane even below the

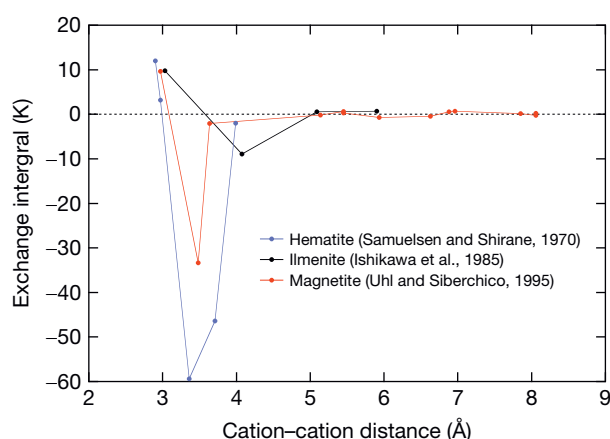


Figure 1 Magnetic superexchange integrals, J_{ij} (K), as a function of cation-cation distance (Å) for hematite (blue), ilmenite (black), and magnetite (red). Data for hematite and ilmenite were measured using inelastic neutron scattering (Ishikawa et al., 1985; Samuelsen and Shirane, 1970). Data for magnetite were calculated using first-principles methods (Uhl and Siberchico, 1995).

Morin transition (Özdemir et al., 2008), although the origin of this so-called 'defect' moment is not fully understood.

In ilmenite, Fe^{2+} and Ti^{4+} are ordered onto A and B (or B and A) layers, and the equivalency of the layers is lost (space group $R\bar{3}$). Since one layer is fully occupied by Ti^{4+} , the strong interlayer interactions that were present in hematite are eliminated. Second-nearest-neighbor interactions extend across the intervening Ti^{4+} layers. These weak negative interactions result in AF ordering below 60 K. The spins in one A layer are then aligned antiparallel to those on the adjacent A layers. Spins are oriented parallel and antiparallel to $[001]$.

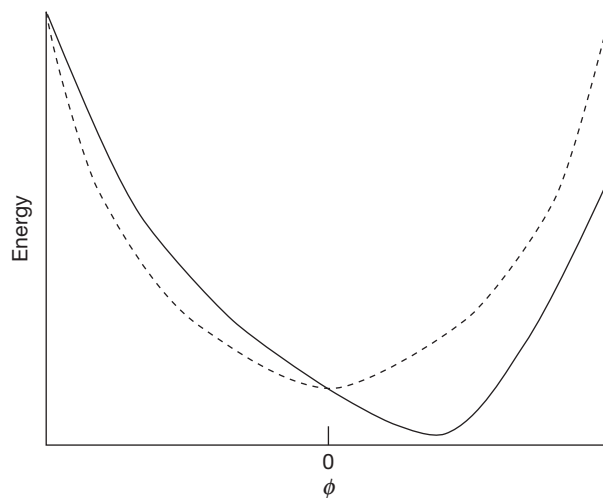


Figure 3 Schematic illustration of the variation in total energy of canted antiferromagnetic hematite with the canting angle, ϕ , as determined by first-principles calculations. Without the inclusion of spin-orbit coupling (dashed line), the energy minimum occurs when the spins are exactly antiparallel to each other ($\phi = 0$). With spin-orbit coupling included (solid line), the energy minimum occurs when the spins are slightly canted with respect to each other ($\phi > 0$). Reproduced from Sandratskii LM and Kübler J (1996) First-principles LSDF study of weak ferromagnetism in Fe_2O_3 . *Europhysics Letters* 33: 447–452, with permission.

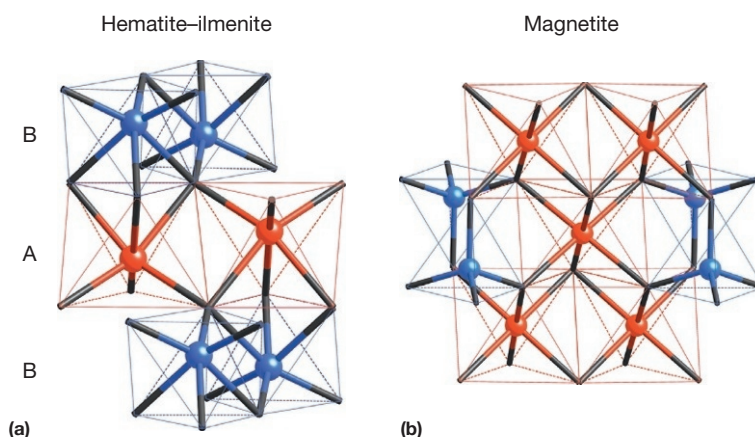


Figure 2 Comparison of the local structural topology of (a) hematite-ilmenite and (b) magnetite. In ilmenite, A layers (red) are occupied by Fe^{2+} and B layers (blue) are occupied by Ti^{4+} (or vice versa). Hematite has the same structural topology, but all layers are occupied by Fe^{3+} . In magnetite, tetrahedral sites (blue) are occupied by Fe^{3+} cations and octahedral sites (red) are occupied by both Fe^{2+} and Fe^{3+} cations.

In magnetite (Figure 2(b)), cations occupy tetrahedral and octahedral interstices within a cubic close-packed oxygen sublattice. Octahedra are occupied by Fe^{2+} and Fe^{3+} cations, whereas tetrahedra are occupied exclusively by Fe^{3+} . Octahedra share edges with adjacent octahedra and corners with adjacent tetrahedra. There are no shared oxygens between adjacent tetrahedra. The first-nearest-neighbor interaction is weak, due to the unfavorable cation–oxygen–cation bond angle (Table 1). The dominant negative tetrahedral–octahedral interaction leads to a ferrimagnetic structure, in which spins on the octahedral sites are antiparallel to those on the tetrahedral sites. Exchange interactions are weak when the two cations are not linked directly by a common oxygen, leading to a weak tetrahedral–tetrahedral interaction and a rapid decrease in interaction strength for cation–cation separations that are greater than ~ 4 Å. Spins point parallel to $\langle 111 \rangle$ above 130 K and parallel to $\langle 100 \rangle$ below 130 K. Below 120–125 K, magnetite undergoes a first-order phase transition (the Verwey transition) to a monoclinic structure (Senn et al., 2012; Walz, 2002). The Verwey transition causes a 15-fold increase in the magnetocrystalline anisotropy of magnetite (Abe et al., 1976) and leads to the development of extensive crystallographic twinning (Bryson et al., 2012; Carter-Stiglitz et al., 2006; Coe et al., 2012; Kasama et al., 2010, 2012; Moloni et al., 1996). Both these effects have a dramatic impact on the magnetic properties of magnetite at low temperatures (Kosterov, 2001; Kosterov and Fabian, 2008; Muxworthy and McClelland, 2000; Smirnov, 2006a,b, 2007; Smirnov and Tarduno, 2002). For further details of the crystal and magnetic structures of minerals, the reader is referred to Banerjee (1991), Dunlop and Özdemir (1997), and Harrison (2000).

2.24.2.2 Atomistic Simulations of Magnetic Ordering

2.24.2.2.1 Theory

Magnetic ordering in minerals was first described using a mean-field model by Néel (1948). For some applications, for example, for estimating Néel temperatures from J_{ij} , this macroscopic approach remains extremely useful (Stephenson, 1972a,b). When studying materials that are heterogeneous at the nanometer scale, however, the mean-field model is inappropriate, and the atomistic nature of the magnetic interactions must be taken into account.

Atomistic simulations are increasingly used to study magnetism at surfaces and interfaces (Dimian and Kachkachi, 2002; Garanin and Kachkachi, 2003; Harrison, 2006; Harrison and Becker, 2001; Harrison et al., 2005, 2007; Kachkachi and Dimian, 2002; Kachkachi and Mahboub, 2004; Kachkachi et al., 2000a,b; Kodama, 1999; Kodama and Berkowitz, 1999; Robinson et al., 2002). They are also well suited to the study of disordered systems, such as spin glasses, that require an atomistic approach to account for frustrated exchange interactions (Charilaou et al., 2011; Harrison, 2009). It is currently practical to describe systems containing $\sim 10^4$ magnetic atoms (Kodama and Berkowitz, 1999). For magnetite, this limitation corresponds to a spherical particle of diameter ~ 8 nm. If surface properties are not of interest, then an effectively infinite (bulk) system can be simulated by creating a large supercell of the crystal structure and applying periodic

boundary conditions (Harrison, 2006, 2009; Mazo-Zuluaga and Restrepo, 2004).

The magnetic energy of such a system is a sum of exchange, anisotropy, magnetostatic, and dipole–dipole interaction terms:

$$E_{\text{mag}} = - \sum_{i \neq j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j - \sum_i K_i (\mathbf{S}_i \cdot \mathbf{e}_i)^2 - (g\mu_B) \sum_i \mathbf{B} \cdot \mathbf{S}_i + E_d \quad [2]$$

where g is the Landé factor, μ_B is the Bohr magneton, $\mathbf{B}$ is an externally applied magnetic field, K is a uniaxial anisotropy constant, $\mathbf{e}$ is the corresponding uniaxial anisotropy axis, and E_d is the demagnetizing energy due to dipole–dipole interactions (Kachkachi et al., 2000a; Kodama and Berkowitz, 1999). E_d can be expressed in the form

$$E_d = \frac{(g\mu_B)^2}{2} \sum_{i \neq j} \frac{(\mathbf{S}_i \cdot \mathbf{S}_j) R_{ij}^2 - 3(\mathbf{S}_i \cdot \mathbf{R}_{ij})(\mathbf{R}_{ij} \cdot \mathbf{S}_j)}{R_{ij}^5} \quad [3]$$

where $\mathbf{R}_{ij}$ is the vector joining atoms i and j . For ellipsoidal particles, eqn [3] simply generates a macroscopic shape anisotropy (Kachkachi et al., 2000a). The large computational overhead involved in summing eqn [3] over all pairs of atoms can be avoided, therefore, by describing this shape anisotropy by a macroscopic approximation of the form

$$E_d = \frac{1}{2V} (D_x M_x^2 + D_y M_y^2 + D_z M_z^2) \quad [4]$$

where D_x , D_y , and D_z are demagnetizing factors and M_x , M_y , and M_z are the components of net magnetization along the principal axes of the ellipsoid (Stacy and Banerjee, 1974). Kachkachi et al. (2000a) found that eqn [4] yielded identical results to eqn [3] for nanoparticles of maghemite ($\gamma\text{-Fe}_2\text{O}_3$). Alternatively, Fourier methods for calculating dipolar interactions can significantly increase computational efficiency (Beleggia, 2004). Different values of K and $\mathbf{e}$ can be specified for atoms in the core and at the surface of a particle. For a surface atom, $\mathbf{e}$ is given by the sum of vectors joining the atom to its nearest neighbors and points approximately perpendicular to the surface (Garanin and Kachkachi, 2003; Kachkachi and Mahboub, 2004; Kodama and Berkowitz, 1999). In this way, the anisotropy is enhanced when the local symmetry is lower than that of the bulk structure. Values for surface anisotropy constants, K , of $\sim 1\text{--}4 k_B/\text{cation}$ (where k_B is the Boltzmann constant) are suggested by electron paramagnetic (PM) resonance measurements of dilute magnetic cations substituted onto low-symmetry sites in nonmagnetic oxides (Low, 1960). Bulk anisotropies are at least two orders of magnitude smaller.

Monte Carlo methods provide an efficient way of determining the equilibrium spin configuration for a given temperature and applied field (Harrison, 2006; Harrison et al., 2007; Kachkachi et al., 2000a; Mazo-Zuluaga and Restrepo, 2004). An atom is chosen at random, and its spin direction changed by a random amount. If the resulting energy change, ΔE_{mag} , is negative, then the change is accepted. If ΔE_{mag} is positive, then the change is accepted with a probability of $\exp(-\Delta E_{\text{mag}}/k_B T)$. After a sufficient number of steps, the system reaches equilibrium. The equilibrium configuration is obtained by averaging over a number of steps until the system converges to the desired statistical significance. In many applications (e.g., for the simulation of hysteresis loops), it is not only the

equilibrium configuration that is important but also the transitional configurations adopted during the approach to equilibrium. In these cases, a dynamic solution to eqn [3] is required. One approach is to use the Landau–Lifshitz–Gilbert (LLG) equation to calculate the trajectory of each spin (Brown, 1963) in the form

$$\frac{dm}{dt} = \gamma m \times H_e - \lambda m \times (m \times H_e) \quad [5]$$

where m is the magnetic moment of a given atom, γ is the gyromagnetic ratio, λ is a damping constant, and H_e is the effective magnetic field acting on that atom:

$$H_e = -\frac{dE_{\text{mag}}}{dm} \quad [6]$$

The first term in eqn [5] describes the precession of the magnetic moment about the effective field direction. The second term decreases the precession angle over time (damping), eventually orienting the magnetic moment along the effective field direction. Although the LLG method has been applied successfully to the study of magnetic nanoparticles (Dimian and Kachkachi, 2002; Kachkachi and Dimian, 2002; Kachkachi and Mahboub, 2004), the method takes many iterations to converge and can often predict unreasonably large coercivities in atomistic simulations due to the large value of the effective exchange field relative to the applied field. Kodama and Berkowitz (1999) adapted the 2-D conjugate direction algorithm of Hughes (1983) to provide a more efficient method of energy minimization for 3-D atomistic simulations (achieving convergence in 5–15 iterations). Whichever method is used, finite temperatures can be modeled by applying random rotations to the spins between energy minimization steps. The magnitudes of rotations are adjusted to give $\Delta E_{\text{mag}} = Nk_B T$, where N is the number of spins in the particle. Random rotations of the individual spins can be combined with random uniform rotations of all of the spins to model collective modes of thermal relaxation, such as superparamagnetism.

The term ‘chemical ordering’ is used to describe changes in the distribution of magnetic and nonmagnetic atoms in a crystal, which may be brought about by both order–disorder and exsolution processes. In homogeneous systems, the coupling between magnetic ordering and chemical ordering can be described by using established thermodynamic models (Burton, 1991; Burton and Davidson, 1988; Ghiorso, 1997; Harrison and Putnis, 1997, 1999; Inden, 1981; Kaufman, 1981). In heterogeneous systems, however, the presence of internal interfaces and phase boundaries necessitates the use of an atomistic approach. The chemical energy of a given atomic configuration can be written in terms of chemical exchange interaction parameters (Bosenick et al., 2001) in the form

$$E_{\text{chem}} = E_0 + \sum_{p,q} N_{p,q} J_{p,q}^{\text{chem}} \quad [7]$$

where $J_{p,q}^{\text{chem}}$ is the energy associated with placing a pair of unlike cations (labeled p) at a given separation (q) within the structure and $N_{p,q}$ is the number of times that each type of pair appears in the configuration. E_0 is constant for a fixed bulk composition and can be neglected. Values for $J_{p,q}^{\text{chem}}$ can be obtained from first-principles or empirical-potential calculations (Becker et al., 2000; Bosenick et al., 2001; Dove, 2001; Vinograd et al., 2004;

Warren et al., 2000a,b) or by calibration with respect to known experimental cation-ordering temperatures (Dang and Rancourt, 1996). A mixture of first-principles and empirical-potential calculations, combined with calibration with respect to well-constrained experimental cation distribution data, has been used to study the systematics of chemical interactions in a range of spinel oxides, including the magnetite–ulvöspinel (Fe_3O_4 – Fe_2TiO_4) solid solution and its Mg analog magnesioferrite–qandilite (MgFe_2O_4 – Mg_2TiO_4) (Harrison et al., 2013; Palin and Harrison, 2007a,b; Palin et al., 2008). Harrison et al. (2000a) used static-lattice calculations to estimate $J_{p,q}^{\text{chem}}$ for the ilmenite–hematite solid solution. These estimates were then refined by fitting the model to cation distribution data obtained using neutron diffraction (Harrison and Redfern, 2001; Harrison et al., 2000b).

In order to simulate coupled magnetic and chemical ordering, a combination of two different Monte Carlo steps must be performed: spin flips and atom swaps. In the spin-flip step, the spin of a randomly chosen atom is changed by a random amount, and the change in magnetic energy, ΔE_{mag} , is used to determine whether this change is accepted or rejected. In the atom-swap step, two atoms are chosen at random and their positions are exchanged. If either atom is magnetic, then the swap will also change the configuration of the spins, and the total energy change, $\Delta E = \Delta E_{\text{chem}} + \Delta E_{\text{mag}}$, is used to determine whether the swap is accepted or rejected. Atom swaps preserve the net spin of the system. Therefore, after a given number of atom swaps, an equal number of spin flips are performed in order to allow the spin configuration to equilibrate with respect to the new atomic configuration. The alternation of atom swaps and spin flips is repeated until the system reaches a state of global equilibrium with respect to both chemical and magnetic degrees of order.

2.24.2.2.2 Application to magnetic nanoparticles

For magnetic nanoparticles with sizes of 1–10 nm, surface atoms (defined as those having fewer nearest neighbors than the bulk structure) make up at least 25% of the total number of atoms. Finite-size and surface effects give rise to magnetic properties that deviate significantly from those of the bulk material (Kachkachi et al., 2000b; Kodama, 1999). The effect of surface anisotropy and surface roughness on the spin structure of 2.5 nm diameter NiFe_2O_4 particles is illustrated in Figure 4 (Kodama, 1999; Kodama and Berkowitz, 1999). Whereas smooth nanoparticles may adopt uniform spin configurations (Figure 4(a) and 4(b)), rough surfaces (characterized by the presence of surface vacancies and broken exchange interactions) typically display surface spin disorder (Figure 4(c) and 4(d)). A number of different surface spin configurations can be adopted, depending on the thermal and field history of the particle. Energy barriers between different surface spin configurations can be very high, leading to high-field irreversibility (Figure 4(c)). In NiFe_2O_4 , for example, hysteresis persists in magnetic fields of up to 16 T (Kodama et al., 1996), implying effective anisotropy fields for surface spins that are ~400 times larger than the bulk magnetocrystalline anisotropy field. The observation of shifted hysteresis loops during field cooling (Kodama et al., 1997) implies that certain surface configurations freeze in preferentially and that there is strong exchange coupling between surface and core spins.

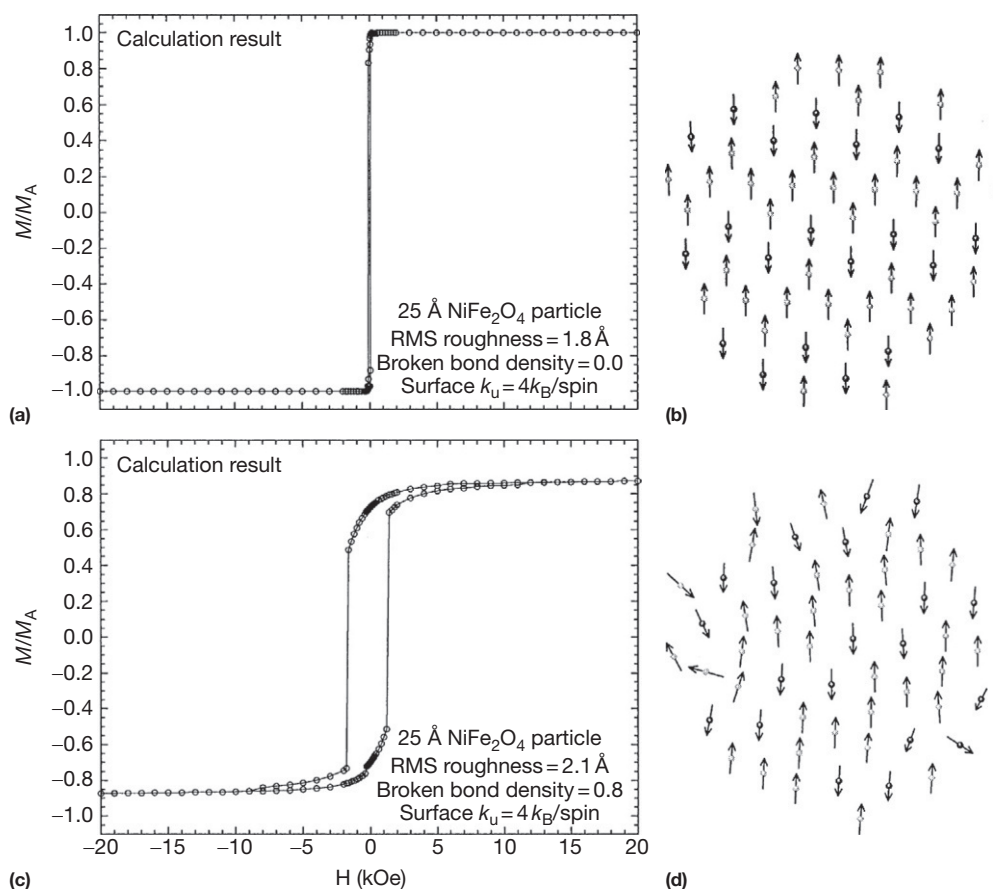


Figure 4 Calculated hysteresis loops and spin configurations of a 2.5 nm diameter spherical particle of NiFe₂O₄. Simulations were performed using an atomistic model of magnetic ordering (Kodama, 1999; Kodama and Berkowitz, 1999). Arrows in (b) and (d) show the spins on individual Fe atoms. Light and dark circles correspond to tetrahedral and octahedral sites, respectively. A particle with no broken bonds and low surface roughness has a low coercivity (a) and no surface spin disorder (b). A particle with a higher broken-bond density and surface roughness displays high coercivity and high-field irreversibility (c), resulting from the presence of significant surface spin disorder (d). Reproduced from Kodama RH (1999) Magnetic nanoparticles. *Journal of Magnetism and Magnetic Materials* 200: 359–372, with permission.

The effect of varying surface anisotropy and exchange coupling on the hysteresis properties of SD ferromagnetic particles has been explored by Kachkachi and Dimian (2002). Significant deviations from the classical Stoner and Wohlfarth (1948) model are observed when the surface anisotropy and exchange constants are of similar magnitude (Figure 5). These deviations are associated with nonuniform reversal mechanisms, which involve the successive switching of surface and core spins.

The magnetic properties of maghemite (γ -Fe₂O₃) nanoparticles have been investigated using both Monte Carlo and conjugate direction methods (Kachkachi et al., 2000a; Kodama and Berkowitz, 1999). Mössbauer spectroscopy indicates that surface spins in maghemite nanoparticles are highly canted (Coey, 1971). Their magnetic properties are dominated by surface effects, which result in high coercive fields, high-field irreversibility, and shifted hysteresis loops in field-cooled samples (Kachkachi et al., 2000a; Tronc et al., 2000). Particles are not saturated in fields of up to 5.5 T (Figure 6(a)), and an anomalous increase in magnetization appears below 70 K (Figure 6(b)), which is more pronounced in smaller particles (Figure 6(c)). The simulated contribution to the magnetization from core and surface spins is illustrated in Figure 7

(Kachkachi et al., 2000a). Assuming that exchange interactions between surface atoms are an order of magnitude weaker than interactions between bulk atoms, an anomalous increase in magnetization observed at low temperatures can be attributed to the ordering of surface spins.

2.24.2.2.3 Application to coupled magnetic and chemical ordering in solid solutions

The magnetic properties of the ilmenite–hematite solid solution are influenced profoundly by nanoscale microstructures resulting from chemical ordering. Slowly cooled rocks that contain finely exsolved hematite–ilmenite have strong and extremely stable magnetic remanence, which may account for some of the magnetic anomalies that are present in the deep crust and on planetary bodies that no longer retain a magnetic field, such as Mars (Brown and McEnroe, 2012; McEnroe et al., 2001, 2002, 2004a,b,c; McEnroe et al., 2009). This remanence has been attributed to the presence of a stable ferrimagnetic substructure, which is associated with the coherent interface between nanoscale ilmenite and hematite exsolution lamellae (the so-called lamellar magnetism hypothesis; Fabian et al., 2008; Harrison, 2006; Harrison and Becker, 2001; Kasama

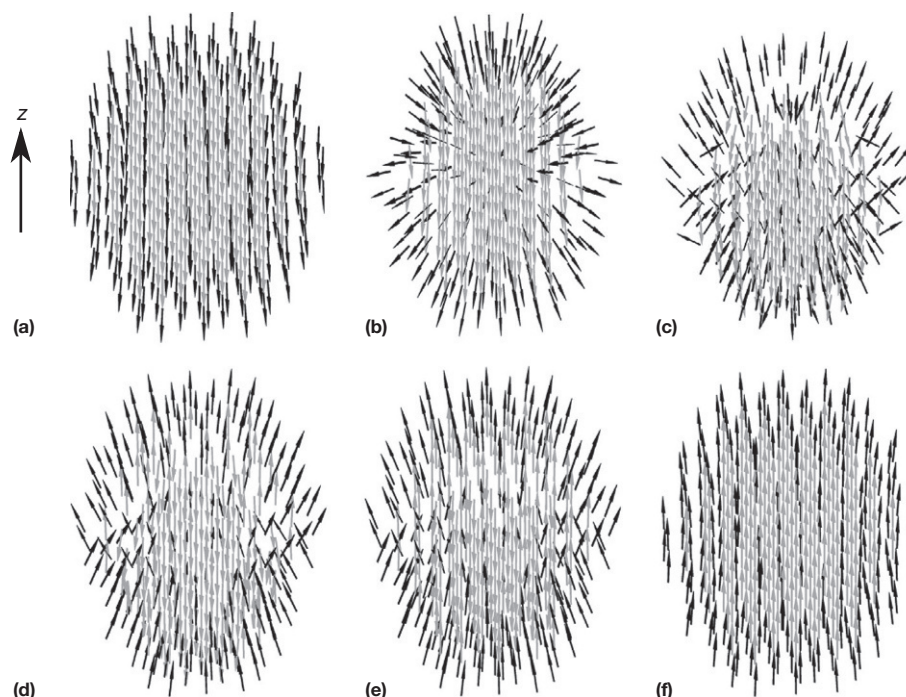


Figure 5 Atomistic simulation of nonuniform magnetic switching in a ferromagnetic nanoparticle with strong surface anisotropy. The spherical particle contains 176 surface spins (dark arrows) and 184 core spins (gray arrows). The easy axis for core spins is parallel to the z -direction (indicated). The easy axis for surface spins is approximately normal to the particle surface. In this example, the core and surface anisotropy constants were chosen to be equal in magnitude, and the exchange integral between neighboring spins was one-tenth the magnitude of the core/surface anisotropy constant. Each spin configuration was obtained at a different value of the applied magnetic field, starting with a saturating field in the negative z -direction (a) and ending with a saturating field in the positive z -direction (f). The surface spins are observed to switch magnetization direction before the core spins (c). Core spins are observed to switch magnetization direction in a cluster-like fashion ((d) and (e)). Adapted from Kachkachi H and Dimian M (2002) Hysteretic properties of a magnetic particle with strong surface anisotropy. *Physical Review B* 66: 174419, with permission.

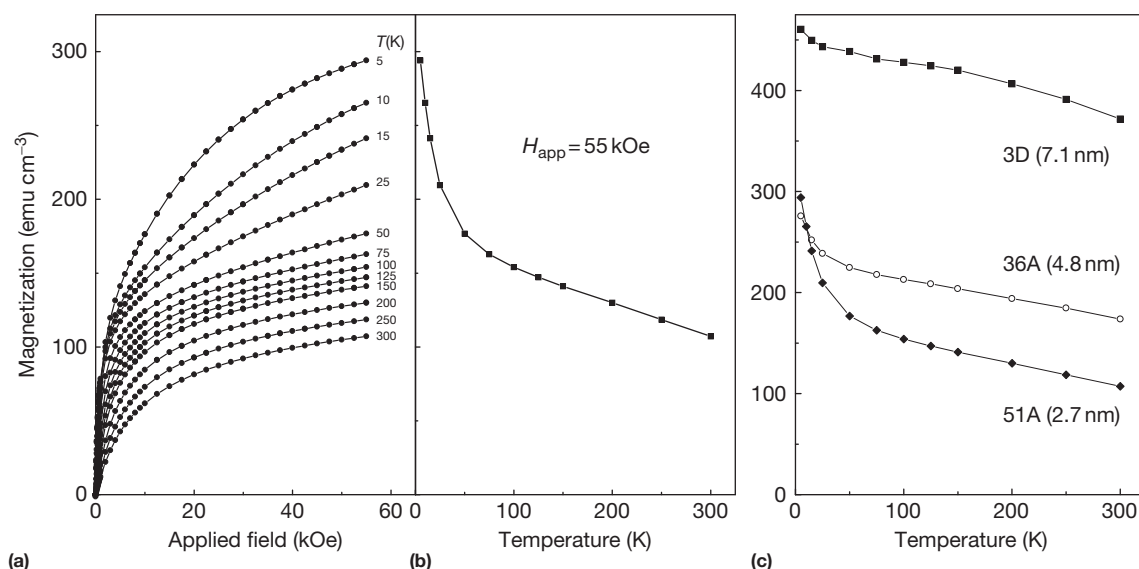


Figure 6 (a) Magnetization of a diluted assembly of γ - Fe_2O_3 nanoparticles, with a mean diameter of 2.7 nm, as a function of magnetic field at different temperatures. (b) Temperature dependence of magnetization at 55 kOe, extracted from (a), showing an anomalous increase in magnetization below 70 K. (c) Temperature dependence of magnetization in a field of 55 kOe for three samples with different mean diameters (2.7, 4.8, and 7.1 nm). The anomalous increase in magnetization at low temperatures is more pronounced in the smaller particles, consistent with a surface effect. Reproduced from Kachkachi H, Ezzir A, Noguès M, and Tronc E (2000) Surface effects in nanoparticles: Application to maghemite γ - Fe_2O_3 . *European Physical Journal B* 14: 681–689, with permission.

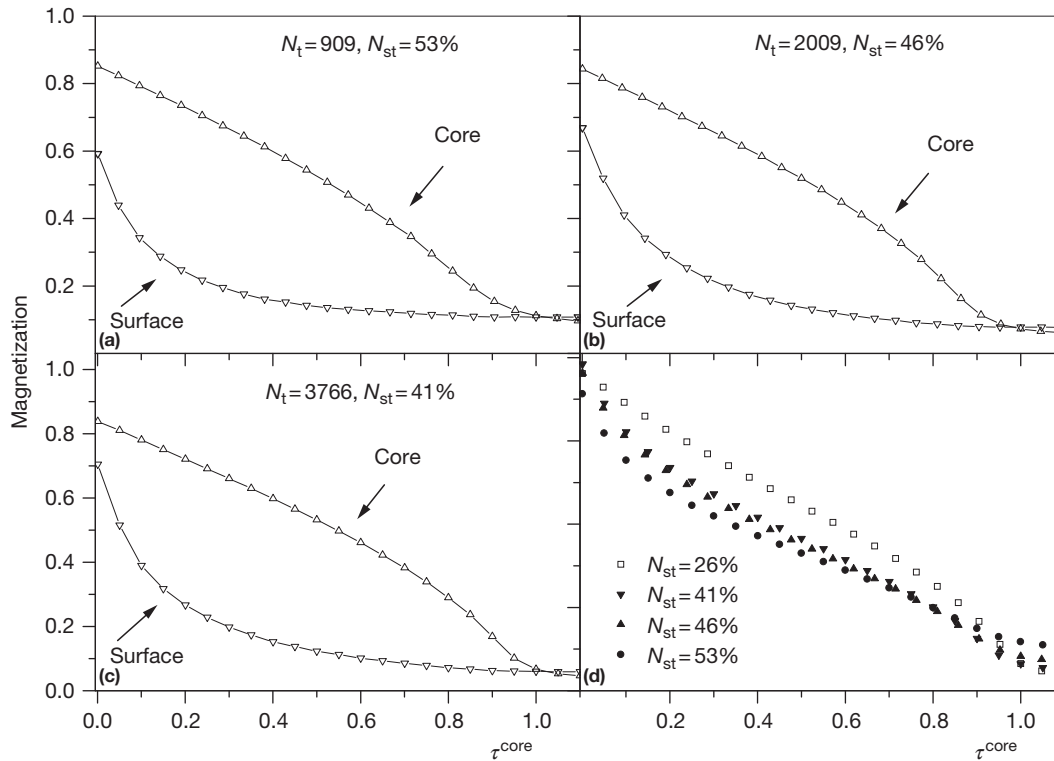


Figure 7 (a)–(c) Temperature dependence of the surface and core magnetization (per site) and (d) mean magnetization, as obtained from atomistic Monte Carlo simulations of an ellipsoidal maghemite nanoparticle. The exchange interactions on the surface are taken to be 1/10 times those in the core, leading to an increase in the surface magnetization contribution at low temperatures. Temperature is given in reduced units ($\tau_c = T/T_c^{\text{core}}$ where T_c^{core} is the critical temperature of the core spins). Reproduced from Kachkachi H, Ezzir A, Noguès M, and Tronc E (2000) Surface effects in nanoparticles: Application to maghemite $\gamma\text{-Fe}_2\text{O}_3$. *European Physical Journal B* 14: 681–689, with permission.

et al., 2003, 2004, 2009; McCammon et al., 2009; Robinson et al., 2002, 2004; Figure 8(a)). Rapidly cooled members of the hematite–ilmenite series, on the other hand, are well known for their ability to acquire self-reversed thermoremanent magnetization (SR-TRM) (i.e., they acquire a remanent magnetization on cooling that is antiparallel to the applied field direction). This phenomenon is related to the presence of fine-scale twin domains that form on cooling through the $R\bar{3}c - R\bar{3}$ cation-ordering phase transition (Bina et al., 1999; Fabian et al., 2011; Hoffman, 1992; Ishikawa and Syono, 1963; Lagroix et al., 2004; Nord and Lawson, 1989, 1992; Prévot et al., 2001; Robinson et al., 2012a,b, 2014; Figure 8(b)).

Harrison (2006) used Monte Carlo simulations to investigate the consequences of coupling between magnetic ordering and chemical ordering in the ilmenite–hematite solid solution (Figure 9). Key features of the equilibrium phase diagram are reproduced successfully by the simulations: (i) a PM to AF transition in the hematite-rich, cation-disordered ($R\bar{3}c$) solid solution; (ii) a PM $R\bar{3}c$ to PM $R\bar{3}$ cation-ordering transition in the ilmenite-rich solid solution; (iii) a PM $R\bar{3}c$ + PM $R\bar{3}$ miscibility gap developing below a tricritical point at $x = 0.58 \pm 0.02$, $T = 1050 \pm 25$ K; and (iv) an AF $R\bar{3}c$ + PM $R\bar{3}$ miscibility gap developing below a eutectoid point at $x = 0.18 \pm 0.02$, $T = 800 \pm 25$ K.

A snapshot of the simulated cation/spin configuration obtained at 100 K for a bulk composition 30% Fe_2O_3 –70% FeTiO_3 (ilm70) is shown in Figure 10. The supercell contains

two nanoscale precipitates of AF $R\bar{3}c$ hematite within a host of PM $R\bar{3}$ ilmenite. The lower precipitate has a thickness of 2 nm (~ 1.5 unit cells), corresponding to the lower size limit of exsolution lamellae typically observed in natural samples (Robinson et al., 2002). The precipitate contains a total of 11 Fe-bearing cation layers: 9 Fe^{3+} layers, which are bounded by mixed Fe^{3+} – Fe^{2+} ‘contact’ layers. The natural tendency for hematite lamellae to form with an odd number of Fe-bearing layers results in the formation of a ‘defect’ moment due to the presence of uncompensated spins (Figure 10(c)). Under favorable conditions, this ‘lamellar magnetism’ far outweighs the spin-canted moment of the hematite phase (Robinson et al., 2004). The upper precipitate has a less well-defined shape and an atomically rough interface with the ilmenite host. It has a thickness of 0.7–1.4 nm (~ 0.5 –1 unit cells), which corresponds to the length scale of the compositional clustering that is commonly observed in natural samples in the vicinity of precipitate-free zones (McEnroe et al., 2002). The more irregular shape and rough interface of the upper precipitate enhances the spin imbalance, yielding a larger net magnetization (Figure 10(d)).

Samples that have cooled rapidly through the $R\bar{3}c - R\bar{3}$ transition develop a high degree of short-range cation order, which is characterized by the formation of fine-scale twin domains (Fabian et al., 2011; Harrison and Redfern, 2001; Nord and Lawson, 1989, 1992; Figure 8(b)). Adjacent domains have an antiphase relationship with each other, in terms of the ordering of Fe and Ti layers; an Fe-rich layer

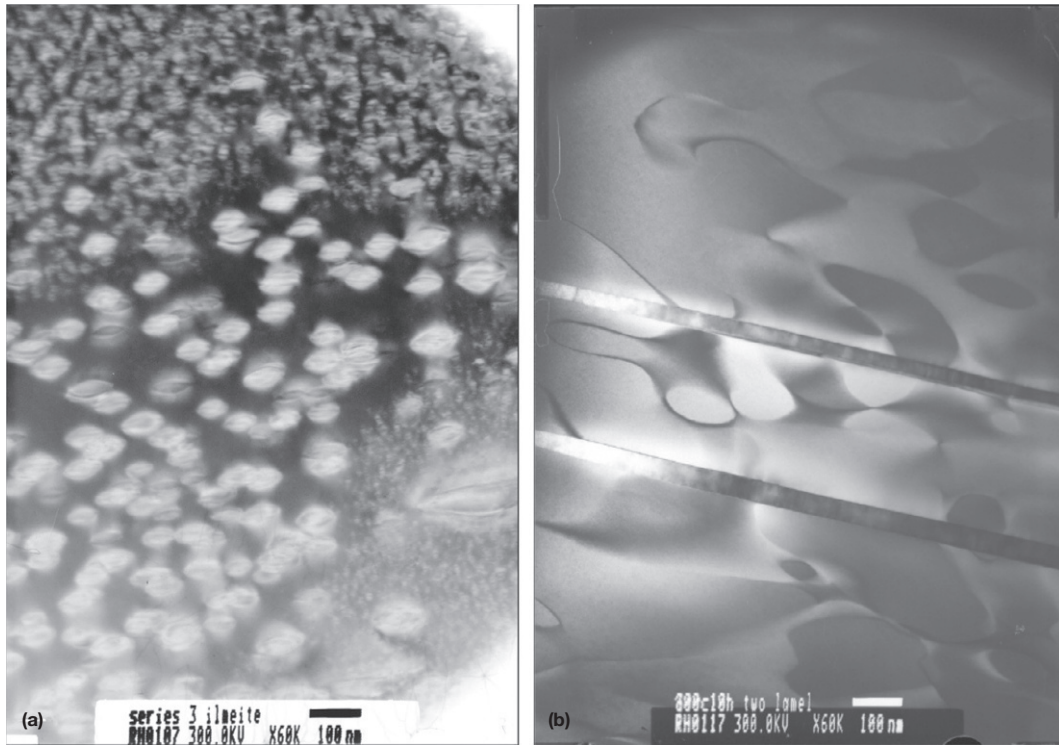


Figure 8 Examples of nanoscale microstructures in the ilmenite–hematite solid solution. (a) A natural hematite–ilmenite containing abundant nanoscale exsolution lamellae of hematite in an ilmenite host (McEnroe et al., 2002). Scale bar = 100 nm. (b) A synthetic sample of the ilmenite–hematite solid solution (ilm70) containing curved antiphase domains (APDs) and antiphase boundaries (APBs), formed after cooling through the $R\bar{3}c$ to $R\bar{3}$ cation-ordering phase transition. The APDs are crosscut by two titanomagnetite lamellae, the result of annealing the sample under slightly reducing conditions. Scale bar = 100 nm.

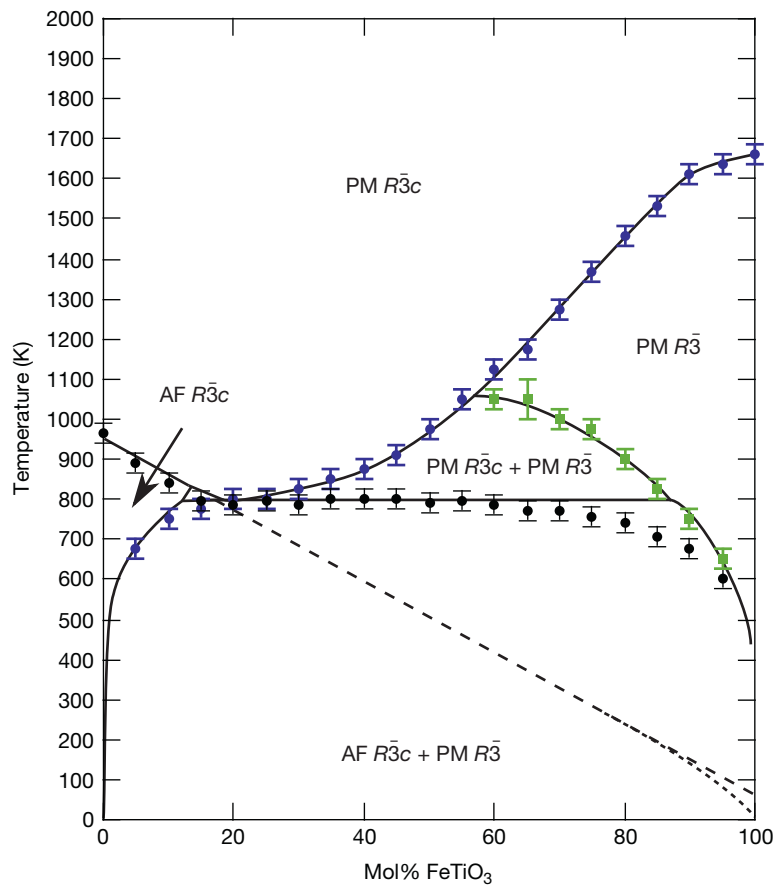


Figure 9 Summary of the equilibrium phase relations in the ilmenite–hematite solid solution determined by Monte Carlo simulation (Harrison, 2006). Dashed and dotted lines show the metastable magnetic ordering temperatures for the cation-disordered and cation-ordered solid solution, respectively.

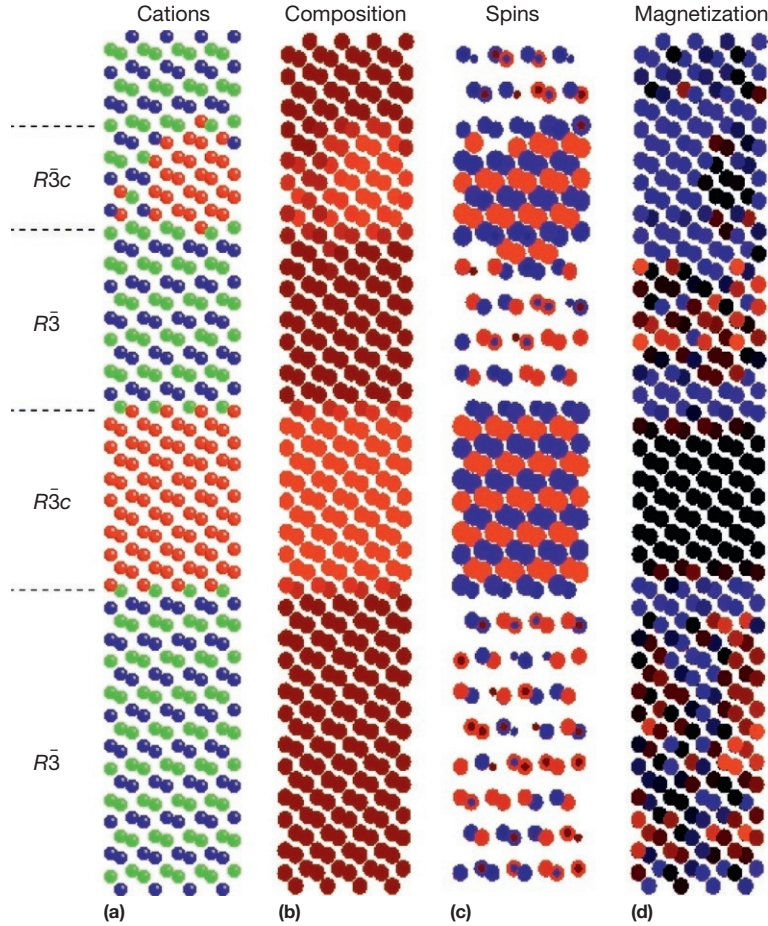


Figure 10 Snapshots of a combined simulation of cation and magnetic ordering in the ilmenite-hematite solid solution (ilm70) at 100 K (Harrison, 2006). (a) Distribution of Fe^{3+} , Fe^{2+} , and Ti (red, green, and blue, respectively). (b) Local chemical composition (red = hematite and black = ilmenite) calculated by averaging the number of Ti cations within the first four coordination shells around each site. (c) Magnitude and direction of spin on each site (red = negative and blue = positive, symbol size proportional to magnitude of spin). (d) Local ferrimagnetic moment (blue = positive and red = negative), calculated by averaging the spin values within the first four coordination shells around each site. The blue regions highlight the ferrimagnetism associated with local spin imbalance at the interface between ilmenite and hematite precipitates.

becomes a Ti-rich layer on crossing the twin wall and vice versa. In order to highlight this relationship, twin domains and twin walls are often referred to as antiphase domains (APDs) and antiphase domain boundaries (APBs), respectively. Figure 11 shows the results of Monte Carlo simulations of a 48-layer supercell of ilm70, with APBs at its center and upper-lower boundaries (Harrison, 2006). The degree of cation order is defined by the order parameter:

$$Q = \frac{N_{\text{Ti}}^B - N_{\text{Ti}}^A}{N_{\text{Ti}}^A + N_{\text{Ti}}^B} \quad [8]$$

where N_{Ti}^A and N_{Ti}^B are the number of Ti^{4+} cations on A and B layers, respectively. The cation/spin configuration after annealing the supercell in the simulation at 850 K is shown in Figure 11(a)–11(d). The APDs are cation-ordered ($Q = \pm 1$) and the APBs are cation-disordered ($Q = 0$) (Figure 11(a)). The APBs are enriched in Fe relative to the APDs, although the magnitude of this enrichment is enhanced by the immiscibility of ilmenite and hematite at this temperature (Figure 11(b)). The spin profile at 25 K shows the presence of oppositely magnetized ferrimagnetic domains, a consequence of the

switch round of Fe-rich and Ti-rich layers at the APB (Figure 11(c)). Experimental confirmation of such negative exchange coupling, obtained using electron holography, is discussed in Section 2.24.3.3.4. The APB shown in Figure 11(c) is characterized by an asymmetric spin profile. Only the very center of the APB can be classed as AF. At 400 K, the majority of the supercell is magnetically disordered, whereas the APBs retain a narrow region of magnetic order (Figure 11(d)).

After annealing at 1100 K, the supercell contains a well-ordered domain and a smaller, less well-(anti)ordered domain (Figure 11(e)). This situation is reached as the system attempts to remove one APD and establish an equilibrium state of homogenous long-range order. Fe enrichment now occurs at the APBs and across the less well-(anti)ordered domain. The spin profile at 25 K indicates a strong ferrimagnetic moment associated with the ordered domain and a weak ferrimagnetic moment with the antioderred domain (Figure 11(g)). At 375 K, magnetic order is lost in the ordered domain, whereas weak magnetic order is retained across the antioderred domain and boundary regions (Figure 11(h)). These properties lead to a self-reversal in the net magnetization on cooling

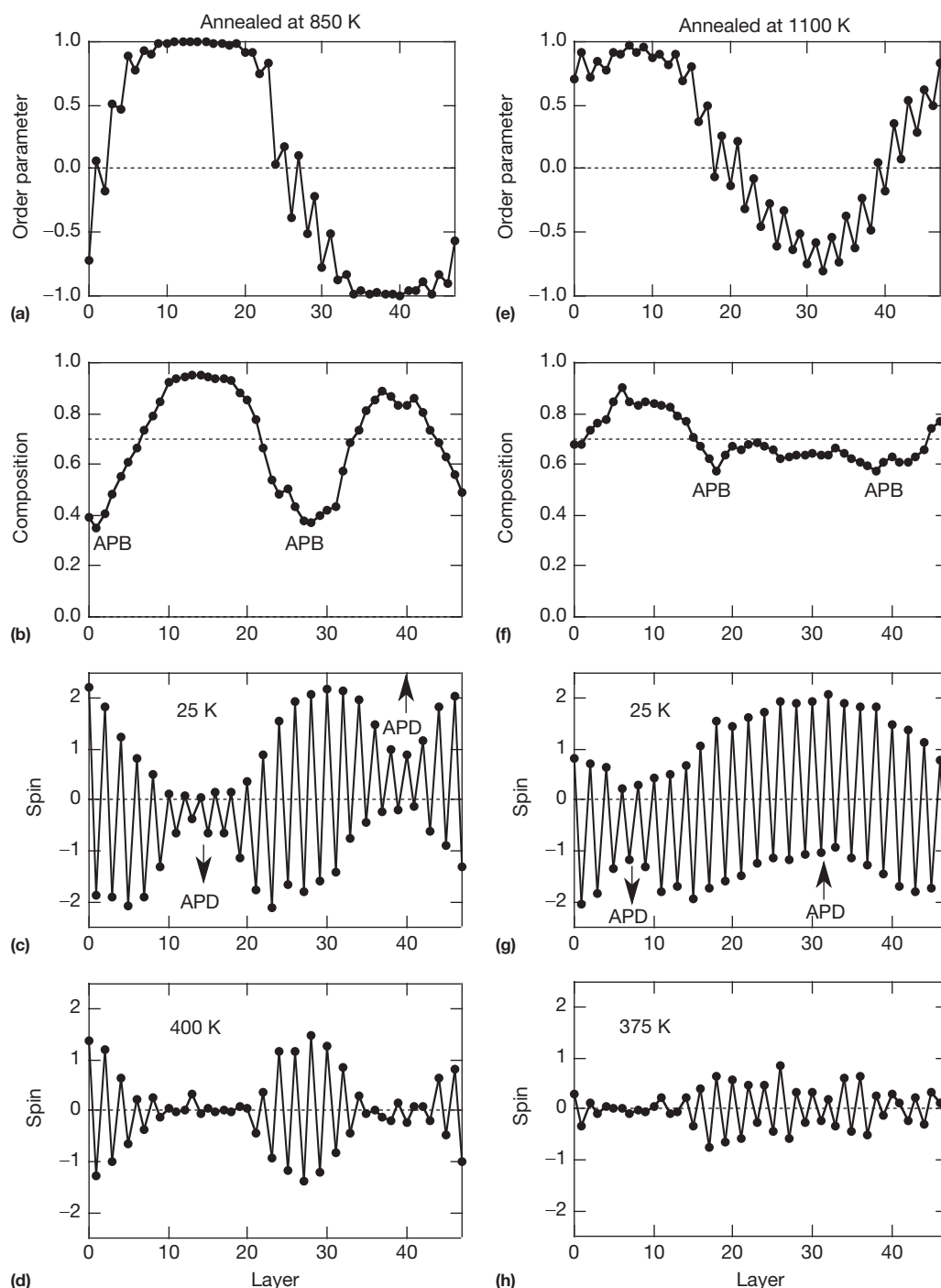


Figure 11 Average values of order parameter, composition, and spin on each of the 48 layers of an $8 \times 8 \times 8$ supercell of ilm70, preannealed at (a–d) 850 K and (e–h) 1100 K (Harrison, 2006; Harrison et al., 2005). A starting configuration with APBs at the bottom and the center of the supercell was chosen in each case. (a) The order parameter profile at 850 K shows two fully ordered–antiferromagnetic APDs ($Q = 1$ and $Q = -1$, respectively) separated by APBs ($Q = 0$). (b) The composition profile at 850 K shows that unmixing has taken place within the PM $R\bar{3}c$ + PM $R\bar{3}$ miscibility gap, with the PM $R\bar{3}$ phase corresponding to the APDs and the PM $R\bar{3}c$ phase corresponding to the APBs. Dashed line indicates the bulk composition, $x = 0.7$. (c) The spin profile at 25 K shows that the APDs are strongly ferrimagnetic. The APD centered on layer 14 has a net negative spin, whereas the APD centered on layer 40 has a net positive spin (indicated by the arrows). (d) The spin profile at 400 K shows that the Fe-rich APBs remain magnetically ordered, whereas the Fe-poor APDs are magnetically disordered. The APBs are associated with a small net spin (see Figure 12). (e) The order parameter profile at 1100 K shows a fully ordered APD ($Q \sim 1$) and a less well-(anti)ordered APD ($Q \sim -0.75$). (f) The composition profile at 1100 K shows that the well-ordered APD has $x > 0.7$, whereas the less well-ordered APD has $x < 0.7$. Evidence for Fe enrichment at the APBs is also seen. (g) The spin profile at 25 K shows that the well-ordered APD is strongly ferrimagnetic, whereas the ferrimagnetic spin of the less well-ordered APD is decreased by the influence of the boundary regions. (h) The spin profile at 375 K shows that the less well-ordered APD and boundary regions are magnetically ordered, whereas the well-ordered APD is magnetically disordered. The magnetically ordered regions carry a small net spin that is opposite to the net spin of the well-ordered APD (see Figure 12).

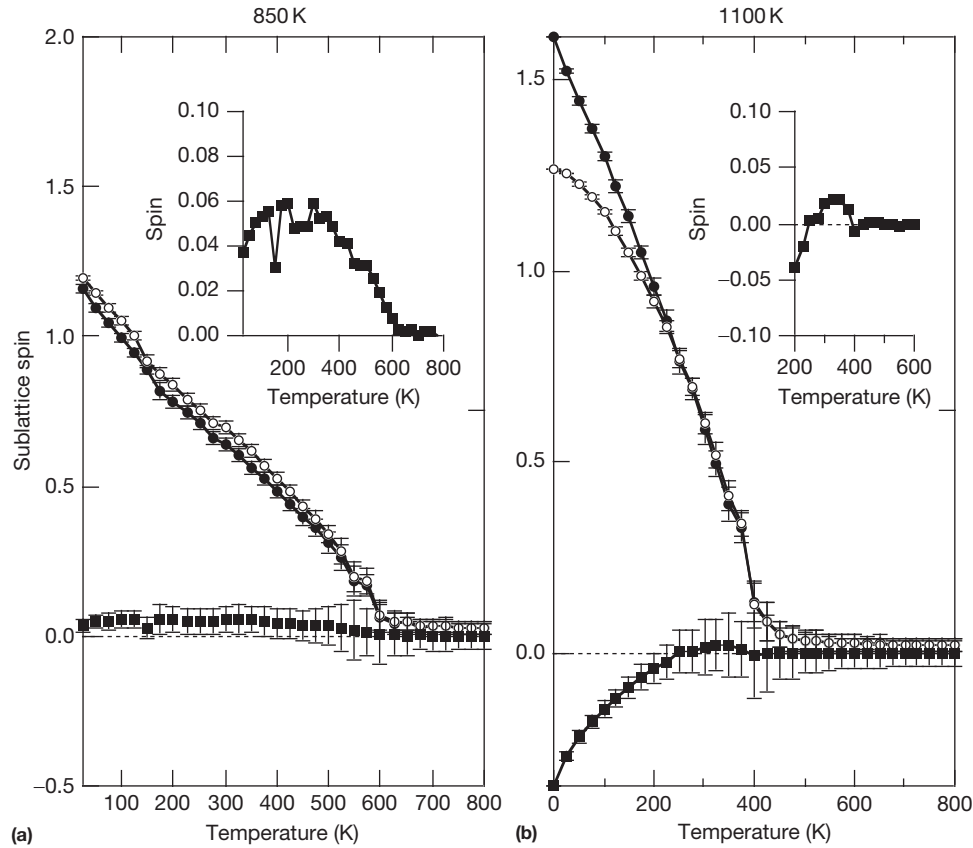


Figure 12 Temperature dependence of sublattice spins S_A and S_B (circles) and net spin $|S_A| - |S_B|$ (squares) for the simulations preannealed at (a) 850 K and (b) 1100 K. Insets show expanded view of the variation in net spin. A self-reversal of the net magnetization occurs in (b) due to the negative exchange coupling between poorly ordered and well-ordered APDs (see Figure 11(e)–11(h)).

(Figure 12). Magnetic ordering in the Fe-enriched antiorordered domain sets in below 425 K, yielding a weak positive ferrimagnetic moment. Magnetic order spreads to the ordered domain on cooling below 350 K. Below 250 K, the moment of the antiorordered domain is outweighed by the oppositely oriented moment of the ordered domain, and the net magnetization reverses. In contrast, no net reversal is observed in the 850 K simulation, which contains equally well-ordered and antiorordered domains, despite the enhanced enrichment of Fe at the APB. The predictions of the atomistic simulation have largely been confirmed by experimental observations (Fabian et al., 2011) and have been developed into a comprehensive theory of self-reversal applicable to much larger microstructural length scales by Robinson et al. (2012 and 2013).

2.24.3 Magnetism at the Nanometer Length Scale

Off-axis electron holography is an advanced TEM technique that allows a 2-D projection of the in-plane component of the magnetic induction in a specimen to be mapped with a spatial resolution approaching the nanometer scale. The high spatial resolution of this technique makes it ideal for the study of magnetic particles that are in the SD to PSD size range, as well as for magnetic minerals that are structurally and/or chemically heterogeneous. Its ability to provide images of stray magnetic fields also makes electron holography an ideal

technique for the study of magnetostatic interactions between magnetic nanoparticles. We begin by reviewing theoretical and practical aspects of electron holography. We then describe its recent application to several different magnetic minerals.

2.24.3.1 Theory of Off-Axis Electron Holography of Magnetic Materials

2.24.3.1.1 Amplitude and phase of a TEM image

The formation of a TEM image can be described in terms of the electron wave function in the image plane of the microscope:

$$\psi(r) = A(r) \exp[i\phi(r)] \quad [9]$$

where A is amplitude, ϕ is phase shift (with respect to a wave that has traveled through vacuum alone), and r is a vector in the plane of the sample (Cowley, 1995). As an electron passes through the microscope, it experiences a phase shift that is associated with both the electrostatic potential of the sample (Figure 13(a)) and the in-plane components of the magnetic induction (Figure 13(b)). In a conventional TEM image, only the spatial distribution of the image intensity,

$$I(r) = \psi(r)\psi^*(r) = A^2(r) \quad [10]$$

is recorded, and all information about the phase shift is lost. Electron holography is an interferometric technique that allows phase information to be recovered. After subtraction

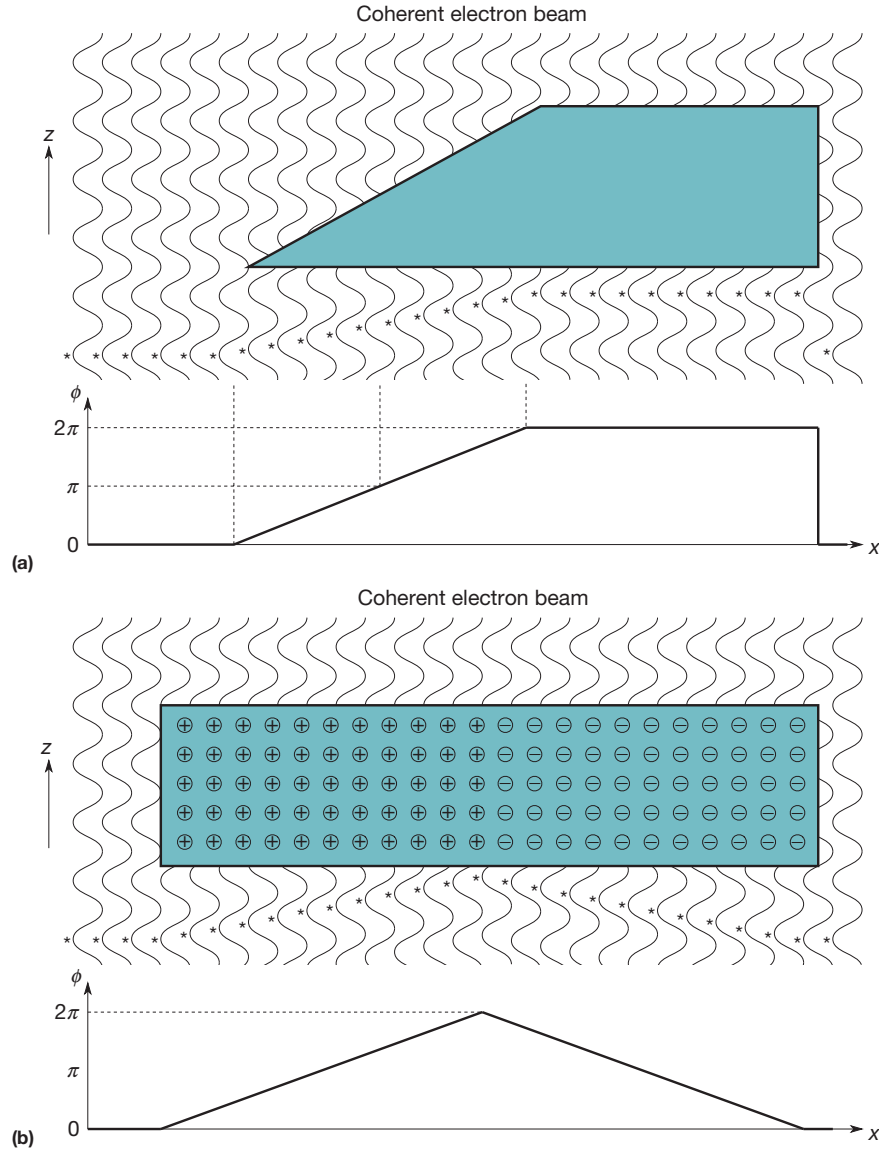


Figure 13 Schematic illustration of the phase shift experienced by electrons passing through a specimen in the TEM. (a) The mean inner potential contribution to the phase shift of electrons passing through a sample of uniform structure and chemical composition reflects changes in the specimen thickness (first term in eqn [13]). (b) The magnetic contribution to the phase shift, given by the second term in eqn [13], reflects the in-plane component of the magnetic induction, integrated along the electron beam direction. For a sample containing two uniformly magnetized domains, one magnetized out of the plane of the diagram (crosses) and one magnetized into the plane of the diagram (dots), the gradient of the phase shift is constant within the domains and changes sign at the domain wall.

of the electrostatic contribution to the phase shift (see in the succeeding text), a phase image can be converted directly into a quantitative 2-D map of the in-plane magnetic induction in the sample (Dunin-Borkowski et al., 2004; Midgely, 2001; Tonomura, 1992; Völkl et al., 1998).

The phase shift (measured relative to that of an electron that has passed through vacuum alone) is given by the expression

$$\phi(x) = C_E \int V_0(x, z) dz - \left(\frac{e}{h}\right) \iint B_{\perp}(x, z) dx dz \quad [11]$$

where x is a direction in the plane of the sample, z is the incident electron beam direction, V_0 is the mean inner potential (MIP), and $B_{\perp}$ is the component of magnetic induction perpendicular

to both x and z (Reimer, 1991). C_E is a constant that depends on the accelerating voltage of the TEM in the form

$$C_E = \left(\frac{2\pi}{\lambda}\right) \left(\frac{E + E_0}{E(E + 2E_0)}\right) \quad [12]$$

where λ is the electron wavelength and E and E_0 are the kinetic and rest mass energies of the incident electrons, respectively. Values of C_E for a range of accelerating voltages are listed in Table 2. If neither V_0 nor $B_{\perp}$ varies with z inside the specimen, and both parameters are zero outside the specimen, eqn [11] can be expressed more simply in the form

$$\phi(x) = C_E V_0(x) t(x) - \left(\frac{e}{h}\right) \int B_{\perp}(x) t(x) dx \quad [13]$$

Table 2 Values of the constant C_E in eqn [12] as a function of TEM accelerating voltage

Voltage (kV)	$C_E (\times 10^6 \text{ rad Vm}^{-1})$
100	9.24396
200	7.2884
300	6.52616
400	6.12141
500	5.87316
600	5.70724
700	5.58974
800	5.50296
900	5.43679
1000	5.38502

where t is the thickness of the sample. Differentiating with respect to x then leads to the expression

$$\frac{d\phi(x)}{dx} = C_E \frac{d}{dx} \{V_0(x)t(x)\} - \left(\frac{e}{h}\right) B_{\perp}(x)t(x) \quad [14]$$

For constant V_0 and t , the first term in eqn [14] is zero, and the gradient of the phase shift is proportional to the desired in-plane component of the magnetic induction in the specimen (Figure 13(b)). The phase gradient can then be written in the form

$$\frac{d\phi(x)}{dx} = -\left(\frac{et}{h}\right) B_{\perp}(x) \quad [15]$$

Unfortunately, in most cases, both V_0 and t vary across the specimen, and careful separation of the magnetic and mean inner potential contributions to the measured phase shift is required before quantitative analysis of the magnetic induction is possible (see Section 2.24.3.1.5).

2.24.3.1.2 Calculation of the mean inner potential

For a specimen that has a single composition and crystallographic orientation, the mean inner potential contribution to the phase shift is proportional to the specimen thickness (Figure 13(a)). Direct measurement of V_0 using electron holography is possible if an independent measurement of the specimen thickness is available. Such measurements are rare, however, and it is often necessary to calculate theoretical values of V_0 . An estimate for V_0 can be obtained by assuming that the specimen can be described as a collection of neutral free atoms (the 'nonbinding' approximation) and by using the expression

$$V_0 = \left(\frac{h^2}{2\pi me\Omega}\right) \sum_{\Omega} f_{el}(0) \quad [16]$$

where $f_{el}(0)$ is the electron scattering factor at zero scattering angle (with dimensions of length), Ω is the unit cell volume, and the sum is performed over all atoms in the unit cell (Reimer, 1991). Calculated values for $f_{el}(0)$ have been tabulated by Doyle and Turner (1968) and Rez et al. (1994). Equation [16] leads to an overestimation of V_0 by $\sim 10\%$, because the redistribution of electrons due to bonding (which typically results in a contraction of the electron density around each atom) is neglected. Calculated upper limits of V_0 for common magnetic oxide minerals are listed in Table 3.

Table 3 Calculated V_0 values for a range of magnetic minerals using eqn [16] and electron scattering factors tabulated by Doyle and Turner (1968)

Mineral name (formula)	V_0 (V)
Hematite (Fe_2O_3)	19.3
Ilmenite (FeTiO_3)	19.9
Magnetite (Fe_3O_4)	19.1
Ulvöspinel (Fe_2TiO_4)	19.1
Maghemite ($\gamma\text{-Fe}_2\text{O}_3$)	17.8
Pseudobrookite (Fe_2TiO_5)	17.3
Ferropseudobrookite (FeTi_2O_5)	17.9

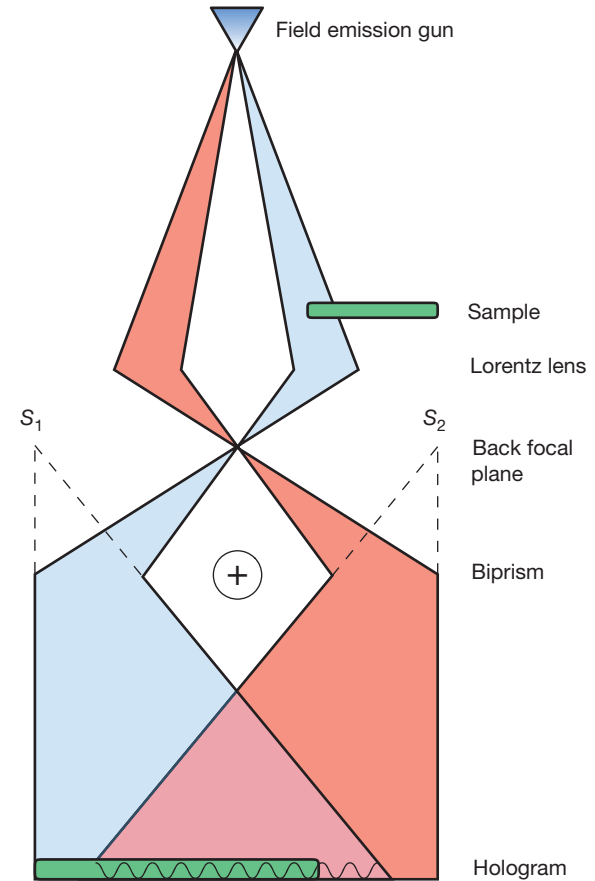


Figure 14 Schematic illustration of the setup used for generating off-axis electron holograms. The sample occupies approximately half the field of view. Essential components are the field-emission electron gun source, which provides coherent illumination, and the positively charged electrostatic biprism, which causes overlap of the sample and (vacuum) reference waves. The Lorentz lens allows imaging of magnetic materials in close-to-field-free conditions.

2.24.3.1.3 Formation of an electron hologram

The microscope setup for electron holography is illustrated schematically in Figure 14. A field-emission gun is used to provide a highly coherent source of electrons. For studies of magnetic materials, a Lorentz lens (a high-strength minilens

located below the lower objective pole piece) allows the microscope to be operated at high magnification with the objective lens switched off and the sample in magnetic field-free conditions. Since a large amount of off-line image processing must be carried out to process holograms and in particular to remove the mean inner potential contribution to the phase shift, there are great advantages in recording holograms digitally, using a charge-coupled device camera.

For off-axis electron holography, the sample is typically placed halfway across the field of view, so that part of the electron wave passes through the sample (the sample wave) and part passes through vacuum (the reference wave). A voltage of 50–200 V is applied to an electrostatic biprism wire (typically a $<1\ \mu\text{m}$ diameter quartz wire coated in Pt or Au) mounted in place of one of the selected area diffraction apertures. This voltage deflects the sample and reference waves, causing them to overlap. If the electron source is sufficiently coherent, then an interference fringe pattern (an electron hologram) is formed in the overlap region. The sample and reference waves can then be considered as originating from two virtual sources, S_1 and S_2 (Figure 14). The angles of the sample and reference waves differ by a small amount, which is proportional to the biprism voltage, and can be described by the wave vector q_c . The intensity in the overlap region is then given by the expression

$$I_{\text{hol}}(\mathbf{r}) = |\psi(\mathbf{r}) + \exp[2\pi i q_c \cdot \mathbf{r}]|^2 \quad [17]$$

$$= 1 + A^2(\mathbf{r}) + 2A(\mathbf{r})\cos[2\pi i q_c \cdot \mathbf{r} + \phi(\mathbf{r})]$$

Hence, an electron hologram consists of a sum of the intensities of the sample and reference waves, onto which is superimposed a set of cosinusoidal fringes with local amplitude A and phase shift ϕ . An example hologram, acquired from a sample containing maghemite inclusions in a matrix of hematite, is shown in Figure 15(a). Local shifts in the positions of the holographic interference fringes, visible in the inset to Figure 15(a), are directly proportional to the phase shift of the electron wave, which results in turn from variations in the thickness, mean inner potential, and magnetic induction of the inclusion and the host. A broader set of Fresnel fringes are also visible at the edges of the hologram in Figure 15(a). These fringes are caused by the edge of the biprism wire.

2.24.3.1.4 Processing of the electron hologram

The sequence of processing steps that is required to extract a phase map, $\phi(\mathbf{r})$, from an electron hologram is illustrated in Figure 15. First, a hologram of the region of interest is acquired (Figure 15(a)). The sample is then moved away from the field of view, and a reference hologram is acquired from a region of vacuum (Figure 15(b)). Next, both the sample and the reference holograms are Fourier-transformed (Figure 15(c)). The Fourier transform of eqn [17] comprises a central peak at $q=0$ and two sidebands at $q=\pm q_c$:

$$FT[I_{\text{hol}}(\mathbf{r})] = \delta(q) + FT[A^2(\mathbf{r})] \\ + \delta(q + q_c) \otimes FT[A(\mathbf{r})\exp(i\phi(\mathbf{r}))] \\ + \delta(q - q_c) \otimes FT[A(\mathbf{r})\exp(-i\phi(\mathbf{r}))] \quad [18]$$

The sidebands contain the Fourier transforms of either the complex image wave or its conjugate. Both amplitude

information and phase information are recovered by isolating one sideband digitally (Figure 15(d)) and performing an inverse Fourier transform of this part of the Fourier transform alone. The diagonal streak at the lower left of Figure 15(d) results from the presence of Fresnel fringes visible in the raw holograms (Figure 15(a) and 15(b)). This streak can lead to artifacts in the reconstructed phase map and is normally masked out (i.e., replaced by pixels with values of zero) before the inverse Fourier transform is performed. The complex image waves that are derived from the sample and reference holograms are divided by each other to remove phase shifts caused by inhomogeneities in the charge and thickness of the biprism wire and distortions caused by aberrations of the microscope lenses and the recording system (de Ruijter and Weiss, 1993). The phase shift is then obtained by evaluating the arctangent of the ratio of the imaginary and real components of the corrected complex image wave (Figure 15(e)). The initial phase map is presented modulo 2π . The 2π discontinuities can be removed by using one of a number of automated phase unwrapping algorithms (Chiglia and Pritt, 1998) to produce an 'unwrapped' final phase image (Figure 15(f)).

2.24.3.1.5 Removing the mean inner potential contribution

If the direction of magnetization in the sample can be reversed exactly, for example, by applying a large magnetic field to the specimen, then the magnetic contribution to the phase shift changes sign in eqn [11]. If phase images that have been acquired before and after magnetization reversal are added together digitally, then the magnetic contribution to the phase shift cancels out, leaving twice the mean inner potential contribution. Magnetization reversal can be performed *in situ* in the TEM by using the magnetic field of the TEM objective lens (Figure 16). The sample is typically tilted to an angle of $\pm 30^\circ$ to the horizontal. The objective lens is then turned on to provide a chosen vertical magnetic field of up to 2 T. The objective lens is then turned off and the sample tilted back to the horizontal prior to acquisition of the hologram. In practice, the two saturation remanent states may not be exactly equal and opposite to each other. It is then necessary to repeat the switching process several times, so that nonsystematic differences between switched pairs of phase images average out. Systematic differences between switched pairs, which can lead to artifacts in the final magnetic induction map, are often identified by inspection. Once the mean inner potential contribution to the phase shift has been determined in this way, it can be subtracted from each individual phase image of the same region of the sample. By varying the magnitude of the applied field, it is possible to record a series of images that correspond to any desired point on the remanent hysteresis loop.

When interpreting the subsequent remanent hysteresis loop, it is important to remember that holography measures the coercivity of remanence (H_{cr}) rather than the coercivity (H_c) of the sample. For SD particles, however, $H_{cr}/H_c \sim 1$, allowing an estimate of the coercivity to be made. A sample with uniaxial anisotropy constant, K , and saturation magnetization, M_s , switches when the vertical field reaches $0.52 B_K$ (assuming a tilt angle of 30° to the horizontal), where $B_K = 2K/M_s$ is the coercivity for fields applied along the anisotropy axis (Stoner and Wohlfarth, 1948).

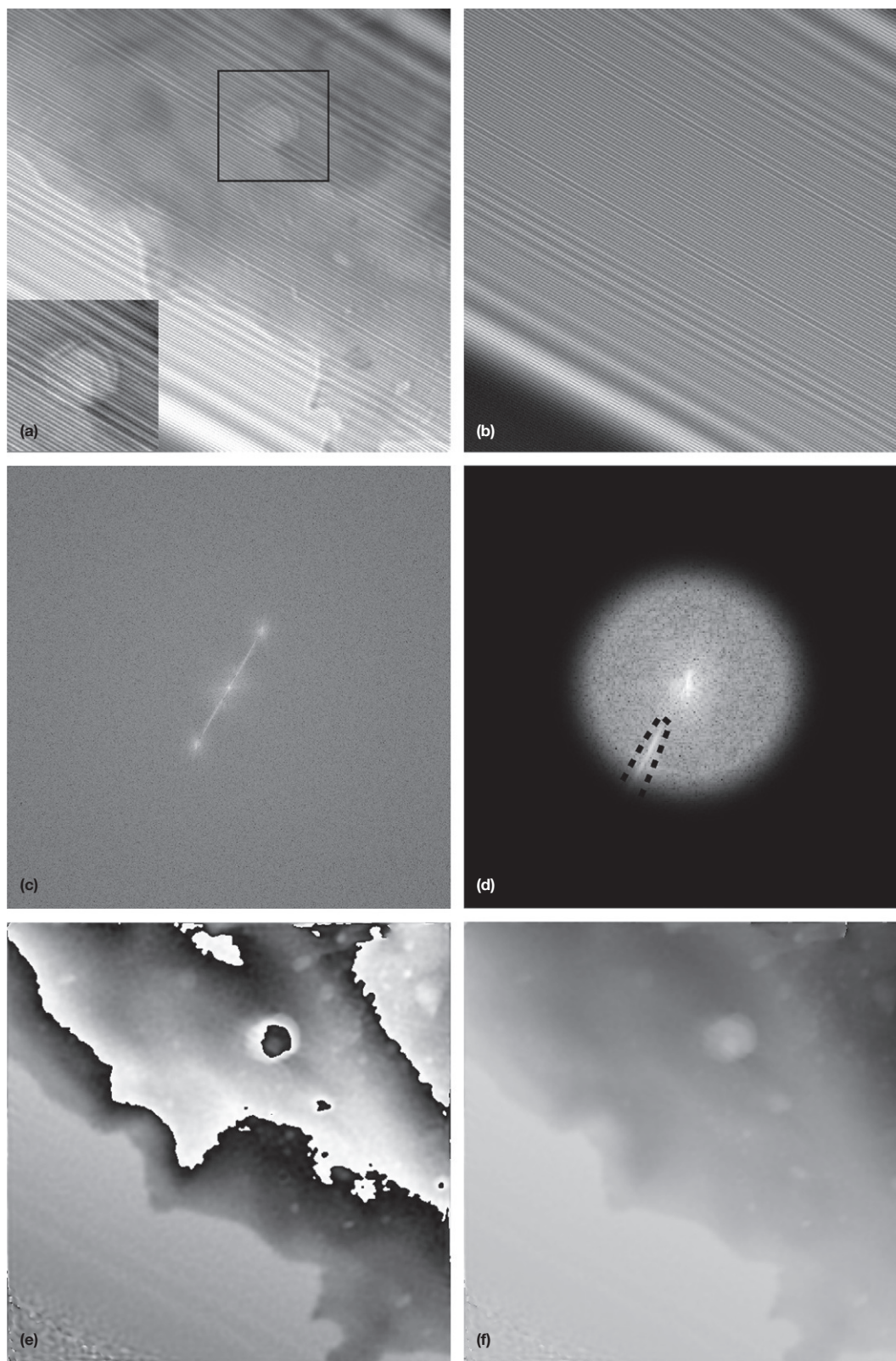


Figure 15 Sequence of image processing steps required to convert an electron hologram into a phase shift image. (a) Original electron hologram of the region of interest (a natural sample of hematite containing nanoscale inclusions of maghemite). Broad Fresnel fringes, caused by the edges of the biprism wire, are visible in the upper right and lower left. The inset is a magnified image of the outlined region, showing the change in position of the fine-scale holographic fringes as they pass through an inclusion. (b) A reference hologram recorded over a region of vacuum. (c) Fourier transform of the electron hologram shown in (a), comprising a central peak, two sidebands, and a diagonal streak due to the Fresnel fringes. (d) A mask is applied to the Fourier transform in (c) in order to isolate one sideband. The Fresnel streak is removed by assigning a value of zero to pixels falling inside the region shown by the dashed line. (e) Inverse Fourier transform of (d) yields the complex image wave, which in turn yields a modulo 2π image of the holographic phase shift. (f) Automated phase unwrapping algorithms are used to remove the 2π phase discontinuities from (e) to yield the final phase shift image.

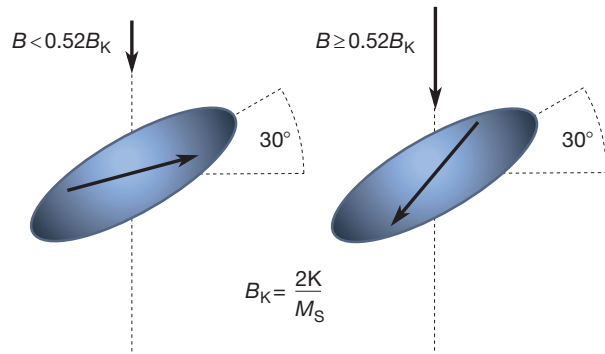


Figure 16 Schematic illustration of magnetic switching in the TEM. A uniaxial particle with anisotropy constant K and saturation magnetization M_s , initially magnetized to the right, is tilted to an angle of 30° to the horizontal. A chosen current is passed through the objective lens of the TEM, exposing the sample to a downward-pointing magnetic field of up to 2 T. The direction of magnetization switches when the vertical field reaches $0.52B_K$, where $B_K = 2K/M_s$. The objective lens is then switched off and the sample is tilted back to the horizontal.

2.24.3.2 Interpretation of Electron Holographic Phase Images

2.24.3.2.1 Quantification of the magnetic induction

A quantitative measure of $B_\perp$, integrated in the electron beam direction, can be obtained from the gradient of the magnetic contribution to the phase shift (eqn [15]). This measurement includes contributions from the internal magnetization of the sample, the internal demagnetizing field, and stray magnetic fields created by the sample in the vacuum surrounding it. For this reason, there is not always an intuitive relationship between the magnetization of the sample and its holographic phase shift. Routine simulation of the phase shift based on a proposed magnetization model is now considered an essential part of holography studies (Beleggia and Zhu, 2003; Beleggia et al., 2003a,b; Bryson et al., 2012; Section 2.24.3.2.4). A simulation of the contributions to the phase shift associated with the presence of a uniformly magnetized 200 nm diameter spherical particle of magnetite is shown in Figure 17. The total phase shift (Figure 17(c)) is the sum of mean inner potential (Figure 17(a)) and magnetic (Figure 17(b)) contributions. An analytic expression that describes the phase shift shown in Figure 17(c), along a line passing through the center of the particle in a direction perpendicular to $B_\perp$, is

$$\phi(x)|_{x \leq a} = 2C_E V_0 \sqrt{a^2 - x^2} + \left(\frac{e}{h}\right) B_\perp \left[\frac{a^3 - (a^2 - x^2)^{3/2}}{x} \right] \quad [19]$$

$$\phi(x)|_{x > a} = \left(\frac{e}{h}\right) B_\perp \left(\frac{a^3}{x} \right) \quad [20]$$

where a is the radius of the particle (de Graef et al., 1999). The mean inner potential and magnetic contributions to this phase profile are shown in Figure 17(d)–17(f). The difference between the minimum and the maximum values of the magnetic contribution to the phase shift in Figure 17(e) is

$$\Delta\phi_{\text{mag}} = 2.044 \left(\frac{e}{h}\right) B_\perp a^2 \quad [21]$$

For a uniformly magnetized cylinder of radius a , the equivalent expression is

$$\Delta\phi_{\text{mag}} = \pi \left(\frac{e}{h}\right) B_\perp a^2 \quad [22]$$

To a good approximation, ion beam-thinned TEM specimens of magnetic materials can often be described locally as plates or wedges of semi-infinite extent in the horizontal plane. If such a sample is magnetized uniformly parallel to its edge, then the effect of demagnetizing and stray fields on the measured phase shift may be negligible, and it may then be possible to determine $B_\perp$ directly by using eqn [15]. This approach requires, however, that the local specimen thickness is known. A measure of the sample thickness can be obtained using energy-filtered imaging (Egerton, 1996). Two images of the sample are acquired: an unfiltered image (formed using both elastically and inelastically scattered electrons) and a zero-loss energy-filtered image. The log of the ratio between the unfiltered and the zero-loss energy-filtered images yields the quantity t/λ_{in} , where λ_{in} is a mean free path for inelastic scattering. Values of λ_{in} can be calculated or measured experimentally (Egerton, 1996; Golla-Schindler et al., 2005). Harrison et al. (2002) determined a value for $\lambda_{\text{in}} = 170$ nm for magnetite. Care is required when using this approach, as the effective magnetic thickness of a sample may be significantly smaller than its physical thickness, due to the presence of magnetically ‘dead’ layers on its surfaces, resulting from specimen preparation techniques such as ion beam thinning. For a sample of known $B_\perp$ and V_0 , an estimate of the thickness of the magnetically dead layers can be obtained by comparing the physical thickness of the specimen derived from the mean inner potential contribution to the phase shift (the first term in eqn [13]) with the magnetic thickness derived from eqn [15]. For an Ar ion-milled synthetic sample of ilm70, assuming a value for $V_0 = 19.6$ V (calculated using eqn [16]) and a saturation induction of 0.225 T, the average difference between the magnetic thickness and physical specimen thickness was found to be ~ 40 nm in total.

2.24.3.2.2 Visualization of the magnetic induction

The in-plane component of the integrated magnetic induction can be visualized by adding contours to the magnetic contribution to the phase shift, as shown in Figure 17(h) in the form of the cosine of the phase image. The spacing of the contours can be varied by multiplying the phase map by a constant before calculating its cosine (an ‘amplification’ factor of 4 was used in Figure 17). By calculating the horizontal and vertical derivatives of the magnetic contribution to the phase shift ($d\phi_{\text{mag}}/dx$ and $d\phi_{\text{mag}}/dy$), a vector field can be determined and displayed in the form of either an arrow map or a color map (Figure 17(j)), whereby the direction and magnitude of the projected in-plane magnetic induction are represented by the hue and intensity of a color, respectively, according to the color wheel shown in Figure 17(l). Color can also be added to the cosine image if desired (Figure 17(k)).

2.24.3.2.3 Quantification of holography images in the general case

Quantitative analysis of the magnetic contribution to the phase shift can, in principle, be used to determine an absolute value for the magnetic moment of a particle. Until recently, such analysis was restricted to uniformly magnetized particles with well-defined shapes (e.g., spheres), for which analytic expressions for the magnetic phase shift can be derived (eqns [19]–[22]; Figure 17). However, a general method for

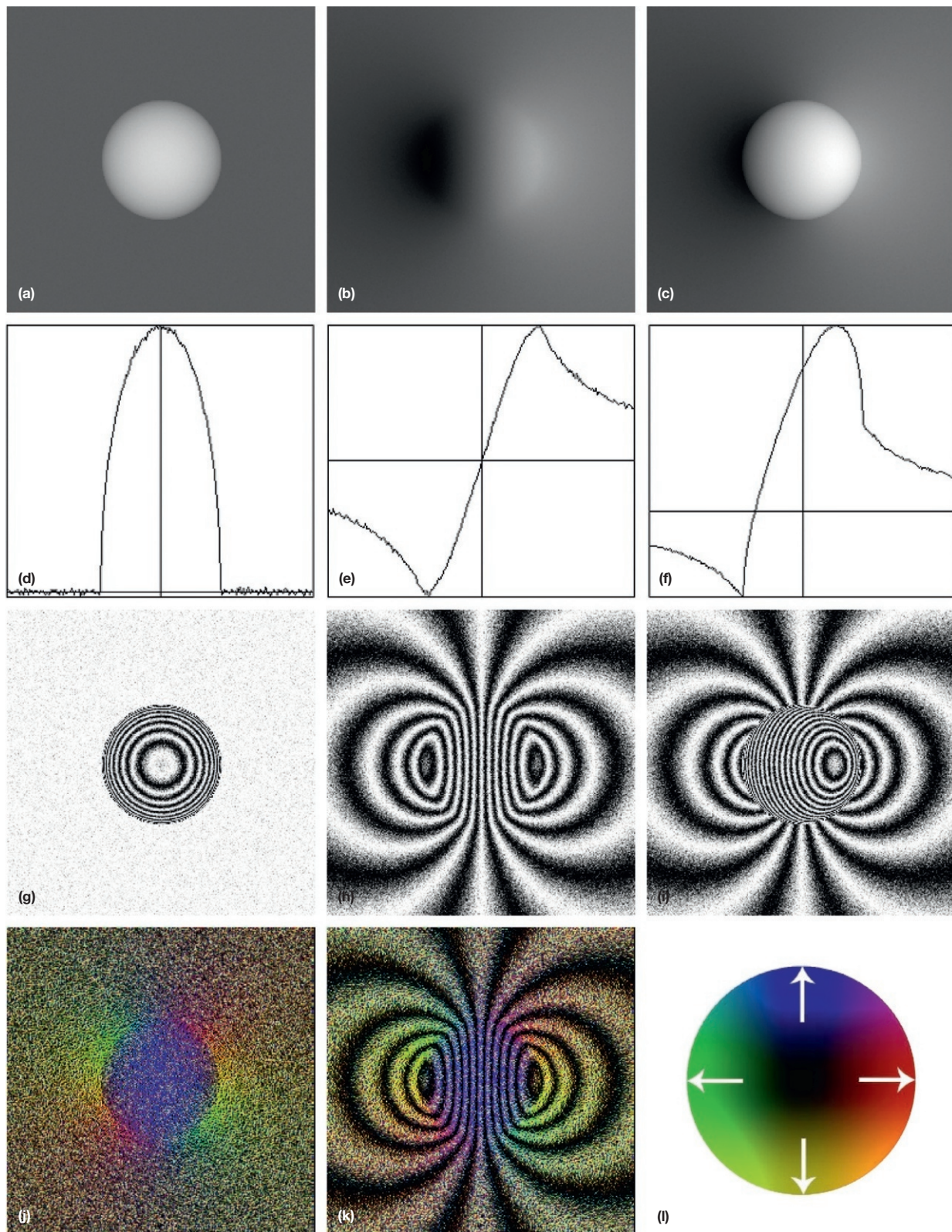


Figure 17 Simulation of the holographic phase shift associated with a 200 nm diameter spherical particle of magnetite. The particle is uniformly magnetized in the vertical direction. The mean inner potential contribution to the phase shift is shown in (a), the magnetic contribution is shown in (b), and the sum of the two is shown in (c). (d–f) Profiles of (a–c), taken horizontally through the center of the particle (i.e., in a direction normal to the magnetization direction). The analytic form of these curves is given by eqns [19] and [20]. (g–i) Cosine of four times the phase shift shown in (a–c). (j) Color map derived from the gradient of the magnetic contribution to the phase shift (b). The hue and intensity of the color indicate the direction and magnitude of the integrated in-plane component of magnetic induction, according to the color wheel shown in (l). The color can be combined with the contour map, as shown in (k).

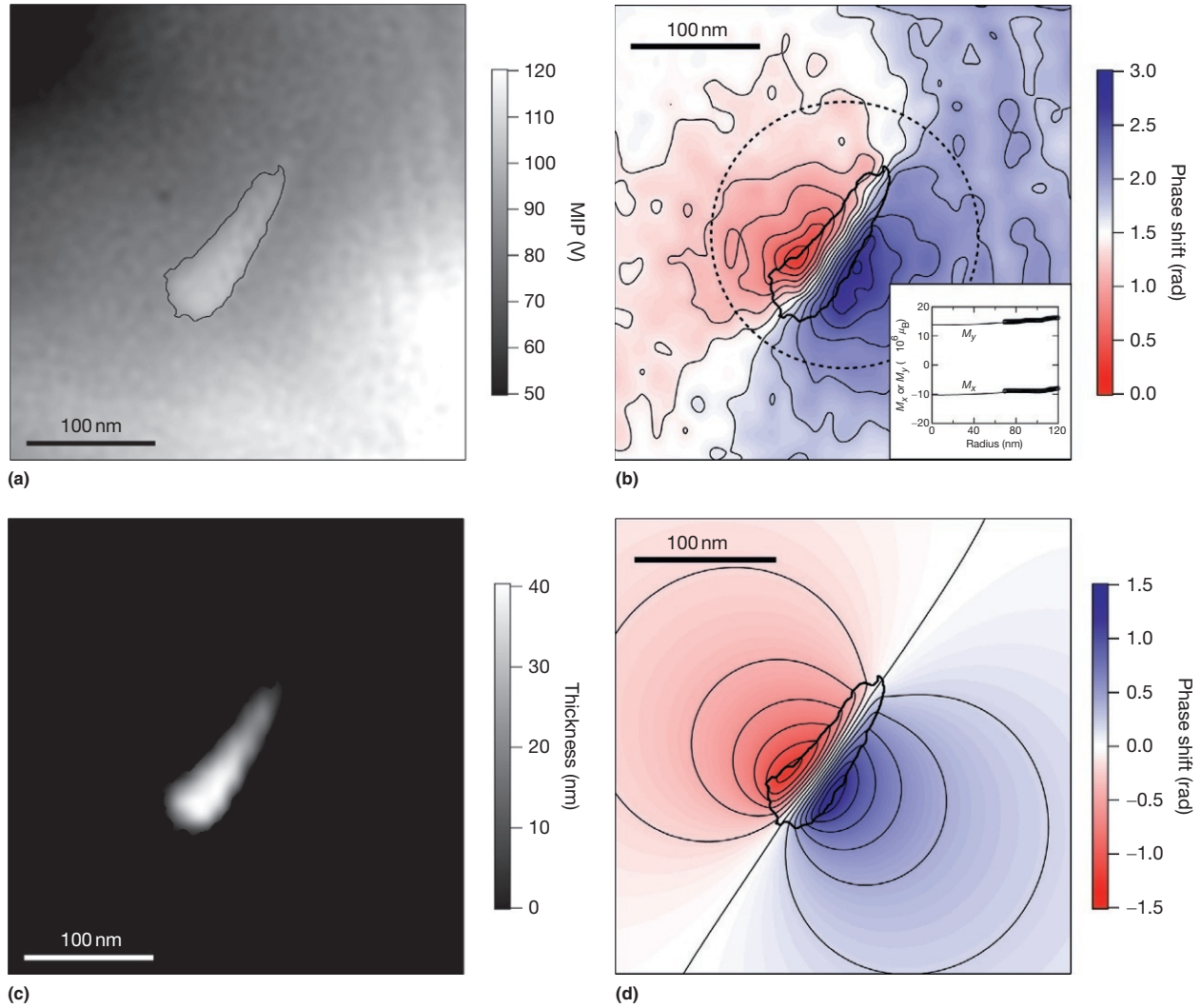


Figure 18 (a) Mean inner potential of an olivine sample containing a metallic Fe inclusion (outlined in black). (b) Magnetic contribution to the phase shift of the metallic Fe inclusion, determined from the difference in the holographic phase shift for two reversed magnetic states (see [Section 2.24.3.1.5](#)). Note the closely spaced phase contours inside the particle, indicating that it is uniformly magnetized along its length, and the dipolar stray fields outside the particle that can be used to determine its magnetic moment. The dashed circle indicates the integration loop used to calculate the total magnetic moment of the particle using the methods outlined in [Section 2.24.3.2.3](#) (eqns [23] and [24]). Inset shows calculations of the x - and y -components of magnetic moment (in μB) for a range of difference integration radii (R_c). Solid lines are quadratic fits to the data, allowing the measurement to be extrapolated to $R_c=0$. (c) Thickness of the metallic particle (nm) projected along the electron beam direction. This image was obtained by first subtracting the background MIP signal from the surrounding olivine, then creating a mask from the particle outline in (a), and finally multiplying the image by a scale factor so that the total sum of the thickness image multiplied by the area per pixel is equal to the volume of the particle (determined by dividing the total magnetic moment of the particle by the known saturation magnetization of Fe). (d) Calculated magnetic contribution to the phase shift based on the projected thickness model from (c), using the method outlined in [Section 2.24.3.2.4](#) (eqn [26]).

measuring the magnetic moment of a particle has now been developed that does not depend on the particle's shape or magnetization state ([Beleggia et al., 2010](#)). The measurement scheme is based on a loop integral of the phase image around a circular boundary containing the structure of interest:

$$M_x = \frac{hR_c}{e\mu_0} \int_0^{2\pi} \phi(R_c \cos \theta, R_c \sin \theta) \cos \theta d\theta \quad [23]$$

$$M_y = \frac{hR_c}{e\mu_0} \int_0^{2\pi} -\phi(R_c \cos \theta, R_c \sin \theta) \sin \theta d\theta \quad [24]$$

where M_x and M_y are the in-plane components of the magnetic moment vector, h is the reduced Planck's constant, R_c is the

radius of the integration circle, e is the electron charge, μ_0 is the permeability of free space, and $\phi(R_c \cos \theta, R_c \sin \theta)$ is the phase shift at a given angle θ around the integration circle.

The method mentioned earlier was successfully employed by Lappe et al. (2011) to measure the magnetic moments of irregularly shaped metallic Fe nanoparticles embedded in a silicate matrix (olivine), thus demonstrating that these particles would have the thermal stability necessary to retain pre-accretionary paleomagnetic remanence in primitive chondritic meteorites. An example of the analysis is shown in [Figure 18](#). The mean inner potential ([Figure 18\(a\)](#)) and magnetic contributions to the phase shift ([Figure 18\(b\)](#)) were determined from reversed pairs of holograms, as described in [Section](#)

2.24.3.1.5. The phase shift around the circumference of a circle enclosing the particle of interest was extracted from the magnetic phase map and integrated to yield M_x and M_y via eqns [23] and [24] (Figure 18(b)). Beleggia et al. (2010) showed that the likely sources of error in this method scale with R_c^2 and hence a measurement of the true moment (M_0) can be obtained by fitting a function of the form $M = M_0 + aR_c^2$ to data obtained over a range of R_c values (inset to Figure 18(b)). If the particles are assumed to be uniformly magnetized with a saturation magnetization $M_s = 1750 \text{ kA m}^{-1}$ (Garrick-Bethell and Weiss, 2010), then the total magnetic moment can be used to calculate the particle volume ($V = M_0/M_s$) and generate a projected thickness model (Figure 18(c)). First, the mean inner potential of the particle is isolated using particle analysis, and the background mean inner potential contribution from the surrounding silicate matrix is subtracted (Figure 18(a)). The isolated mean inner potential signal (which is proportional to the particle thickness) is then multiplied by a calibration factor so that the integral of the mean inner potential is equal to V (Figure 18(c)). Given M_x , M_y , and t , the holographic phase shift can then be simulated using the methods outlined in Section 2.24.3.2.4 (Figure 18(d)).

2.24.3.2.4 Simulation of holography images in the general case

General Fourier methods for the calculation of the magnetic phase shift are derived by Beleggia and Zhu (2003) and Beleggia et al. (2003a,b). These methods have been incorporated into a convenient software package ATHLETICS by Bryson et al. (2012), which automates the simulation of electron holography images (<http://www.esc.cam.ac.uk/research/research-groups/athletics>) for nonuniformly magnetized samples. The real space variation in magnetic moment, $M(r)$, can be written in the form

$$M(r) = M_0 m(r) \quad [25]$$

where $m(r)$ is a unit vector. Beleggia and Zhu (2003) derived the magnetic phase shift in reciprocal space from the Fourier transform of $m(r)$:

$$\phi_m(k) = \frac{i\pi B_0}{\phi_0 k_{\perp}^2} (m(k_x, k_y, 0) \times k) \cdot z \quad [26]$$

where $B_0 = \mu_0 M_0$ is the saturation induction, ϕ_0 is the flux quantum ($h/2e = 2.07 \times 10^3 \text{ T nm}^3$), $m(k)$ is the Fourier transform of $m(r)$, and $k_{\perp} = (k_x^2 + k_y^2)^{1/2}$. The phase of an electron wave exiting a sample is evaluated as follows. The x and y components of $m(r)$ are multiplied by the thickness to create two 2-D 'magnetic thickness' matrices $m_x(x,y)$ and $m_y(x,y)$. The fast Fourier transform (FFT) of m_x and m_y is calculated and $\phi_m(k)$ is evaluated via eqn [26]. The inverse FFT of $\phi_m(k)$ then yields $\phi_m(x,y)$. The application of this method is shown in Figure 18(d), demonstrating excellent quantitative agreement between observed and simulated magnetic signals.

2.24.3.3 Experimental Results

2.24.3.3.1 Electron holography of isolated magnetite crystals

An experimental study of isolated magnetic nanoparticles allows the effects of particle size, shape, and

magnetocrystalline anisotropy on their magnetic state to be assessed without the complicating influence of magnetostatic interactions. Magnetotactic bacteria provide a convenient source of high-purity, relatively defect-free magnetite crystals with varying morphologies, aspect ratios, and sizes in the range 10–200 nm (Arató et al., 2005; Bazylinski and Frankel, 2004; Devouard et al., 1998). Although magnetotactic bacteria normally grow crystals in closely spaced chains, the preparation of bacteria for TEM examination by air-drying inevitably leads to cell damage and a degree of chain breakup. Figure 19(a) shows a high-resolution TEM image of an isolated 50 nm magnetite crystal from a bacterial cell. This crystal was separated by at least 500 nm from adjacent crystals. The 3-D morphology and orientation of the crystal were determined by using electron tomography, from a series of 2-D high-angle annular dark-field images taken over an ultrahigh range of tilt angles (Figure 19(b)). The tomographic reconstruction reveals that the particle is elongated slightly in the [111] direction in the plane of the specimen (as indicated by the white arrow in Figure 19(a)). The crystallographic orientation of the particle is shown in the form of a stereogram in Figure 19(e).

Electron holography of the magnetite crystal was performed both at room temperature (Figure 19(c)) and at 90 K (Figure 19(d)). The magnetic contribution to the phase shift was isolated by performing a series of *in situ* magnetization reversal experiments, as described in Section 2.24.3.1.5. The direction of the in-plane component of the applied field is indicated by the black double arrow. Both images show uniformly magnetized SD states, including the characteristic return flux of an isolated magnetic dipole (Figure 17(k)). In both cases, the remanent magnetization direction appears to make a large angle to the applied field direction. At room temperature, the phase contours in the crystal make an angle of $\sim 30^\circ$ to the [111] elongation direction (Figure 19(c)). The contours are parallel to the [111] elongation direction at 90 K (below the Verwey transition; Figure 19(d)).

Figure 20(a) shows a profile of the magnetic contribution to the phase image that was used to create Figure 19(c), taken along a line passing through the center of the crystal in a direction perpendicular to the phase contours. A least squares fit of the experimental profile to eqns [19] and [20] yielded a value for $B_{\perp}$ of $0.6 \pm 0.12 \text{ T}$. This value is equal to the room-temperature saturation induction of magnetite, suggesting that the magnetization direction of the particle lies exactly in the plane of the specimen, close to the [131] crystallographic direction (Figure 19(e)). This direction corresponds to the longest diagonal dimension of the particle, which is consistent with shape anisotropy dominating the magnetic state of the crystal at room temperature. The 90 K phase profile (Figure 20(b)) yielded a value for $B_{\perp}$ of $0.46 \pm 0.09 \text{ T}$. This value is lower than the saturation induction of magnetite at 90 K, suggesting that, at remanence, the magnetization direction in the crystal is tilted out of the plane by $\sim 40^\circ$ to the horizontal. This direction is close to either [210] or [012] (Figure 19(e)). Below the Verwey transition, the magnetocrystalline anisotropy of magnetite is known to increase considerably in magnitude (Abe et al., 1976; Muxworthy and McClelland, 2000) and to switch from $\langle 111 \rangle_{\text{cubic}}$ to $\langle 001 \rangle_{\text{monoclinic}}$. The $\langle 001 \rangle_{\text{monoclinic}}$ easy axis can lie along any one of the original $\langle 100 \rangle_{\text{cubic}}$ directions. Both the [100] and the [001] directions of the original cubic crystal lie close to the observed remanence direction,

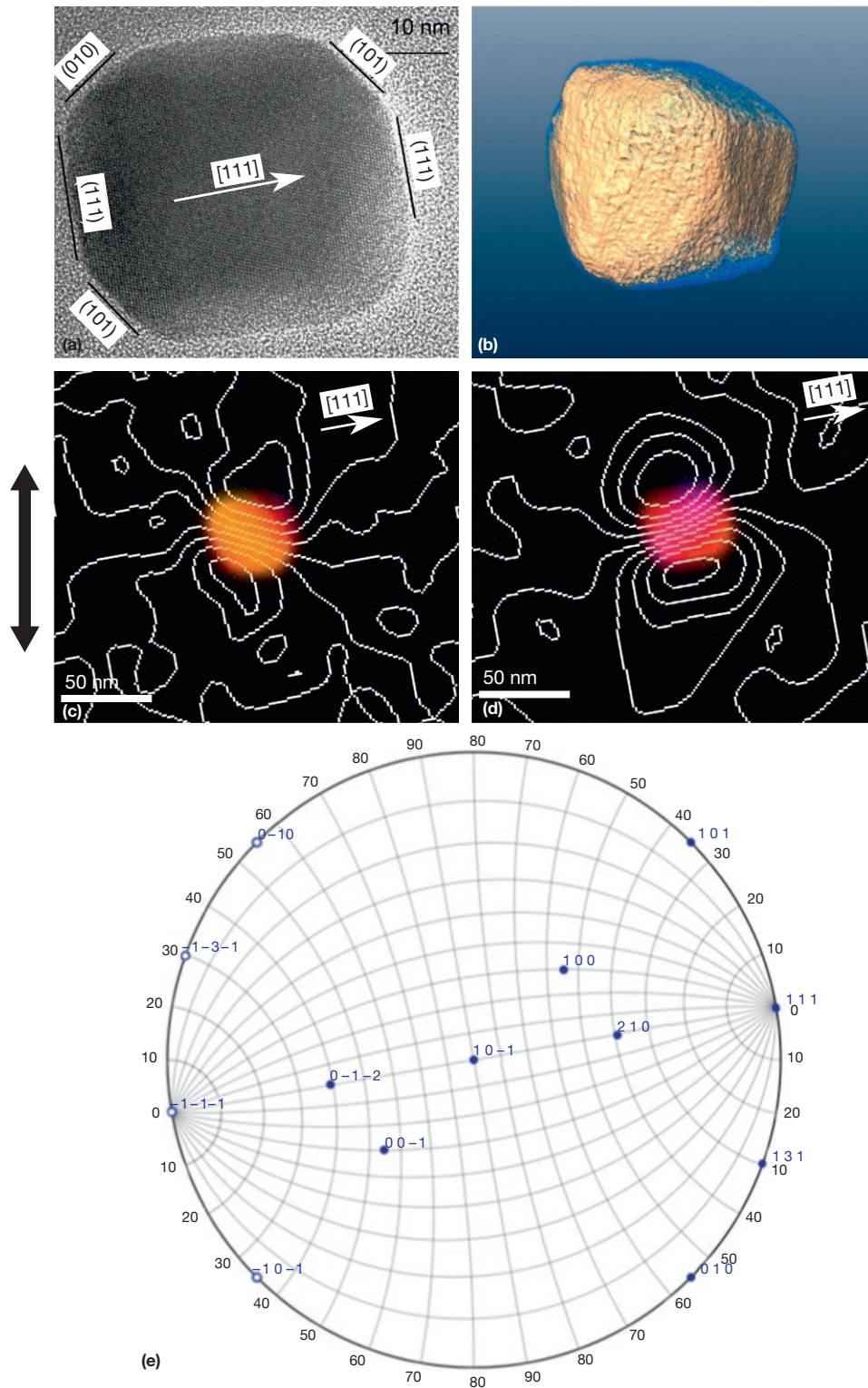


Figure 19 (a) High-resolution image of a 50 nm diameter magnetite crystal from a magnetotactic bacterium (image courtesy of M. Pósfai). (b) 3-D reconstruction of the same particle, obtained using electron tomography (image courtesy of R. Chong). (c and d) Remanent states of the particle at room temperature and 90 K, respectively. The remanent states were obtained after tilting the sample to $\pm 30^\circ$ in the vertical 2T field of the TEM objective lens. The in-plane component of the applied field was directed along the black double arrow. (e) Stereographic projection showing the crystallographic orientation of the sample. At room temperature, the remanent magnetization direction is close to [131]. At 90 K, the remanent direction is close to either [210] or [012].

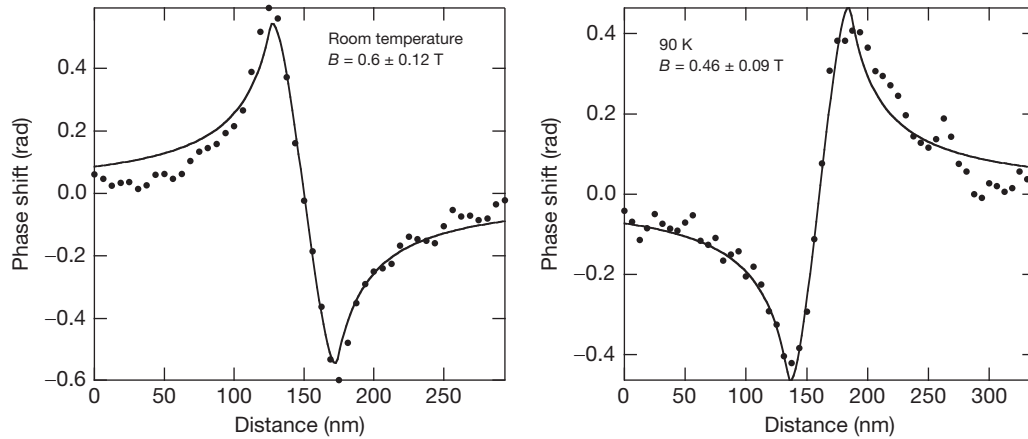


Figure 20 Profiles of the magnetic contribution to the phase shift across the magnetite particle shown in Figure 19 at (a) room temperature and (b) 90 K (closed circles). Profiles were taken through the center of the particle in a direction normal to the contours shown in Figure 18(c) and 18(d). Solid lines are least squares fits to the data using eqns [19] and [20], yielding $B_{\perp} = 0.6 \pm 0.12 \text{ T}$ at room temperature and $B_{\perp} = 0.46 \pm 0.09 \text{ T}$ at 90 K.

suggesting that magnetocrystalline anisotropy has a more significant impact on the remanence direction than shape anisotropy at 90 K. The fact that the remanence direction in Figure 19(d) is perpendicular to the applied field direction suggests that this choice may be influenced by the morphology of the crystal.

Theoretical predictions of the effect of particle size and shape on the magnetic state of magnetite are shown in Figure 21 (Butler and Banerjee, 1975; Muxworthy and Williams, 2006). The upper solid line shows the theoretical boundary between SD and two-domain states (Butler and Banerjee, 1975). The dashed line shows the boundary between SD and single-vortex (SV) states predicted by micromagnetic simulations (Muxworthy and Williams, 2006; see Section 2.24.4). For equidimensional particles, the equilibrium SD–SV transition is predicted to occur at a particle size of 70 nm (Fabian et al., 1996; Williams and Wright, 1998) and the transition to a superparamagnetic (SP) state is observed to occur below 25–30 nm (Dunlop and Özdemir, 1997). The observation of a stable SD state for the roughly equidimensional 50 nm crystal in Figure 19 is in agreement with the expected behavior.

2.24.3.3.2 Electron holography of chains of closely spaced magnetite crystals

Figure 22(a) and 22(b) shows a bright-field TEM image and a 3-D tomographic reconstruction, respectively, of a double chain of magnetite crystals from a magnetotactic bacterial cell (Simpson et al., 2005). Each crystal has its [111] crystallographic axis aligned accurately (to within 4°) of the chain axis, as shown by the arrows in Figure 22(a), but is rotated by a random angle about this axis (like beads on a string). From a magnetic perspective, the alignment of the crystals ensures that their room-temperature magnetocrystalline easy axes are closely parallel to the chain axis. The largest crystals are elongated slightly along [111], with lengths of 92–94 nm and widths of 82–88 nm. Isolated crystals of this size would be expected to adopt SV states at equilibrium (Figure 21). Electron holography of similar chains revealed, however, that such crystals are magnetized uniformly parallel to each chain axis (Figure 22(c)). For such highly aligned chains of

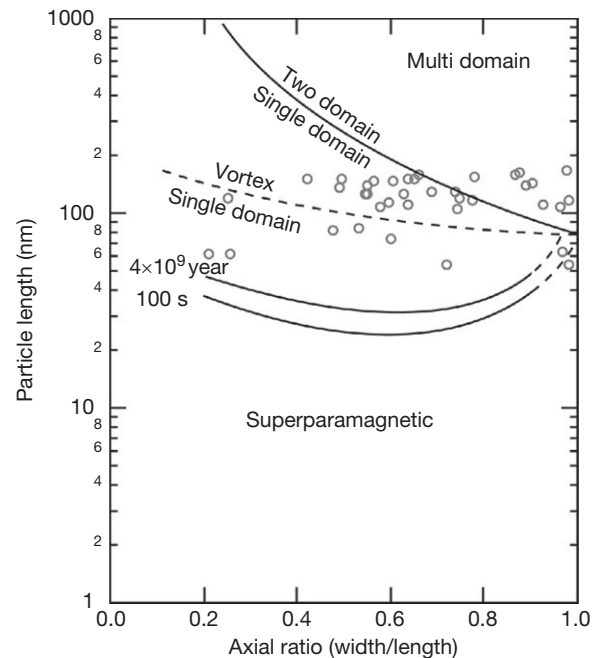


Figure 21 Equilibrium threshold sizes for SP, SD, SV, and two-domain magnetic states as a function of particle length and axial ratio. Upper solid line shows the calculated boundary between SD and two-domain states (Butler and Banerjee, 1975). Lower solid lines show the sizes for SP behavior with relaxation times of $4 \times 10^9 \text{ years}$ and 100 s (Butler and Banerjee, 1975). Dashed line shows the boundary between SD and SV states for uniaxial ellipsoidal particles, calculated using finite element micromagnetic methods (Muxworthy and Williams, 2006). Open circles show the sizes and aspect ratios of the magnetite blocks from region B in Figure 25.

crystals, magnetostatic interactions move the boundary between SD and SV states to larger particle sizes and promote the stability of SD states. This effect, which is also predicted by micromagnetic simulations (Muxworthy and Williams, 2006; Muxworthy et al., 2003a; see Section 2.24.4), enables bacteria to grow SD crystals to much larger sizes than would otherwise

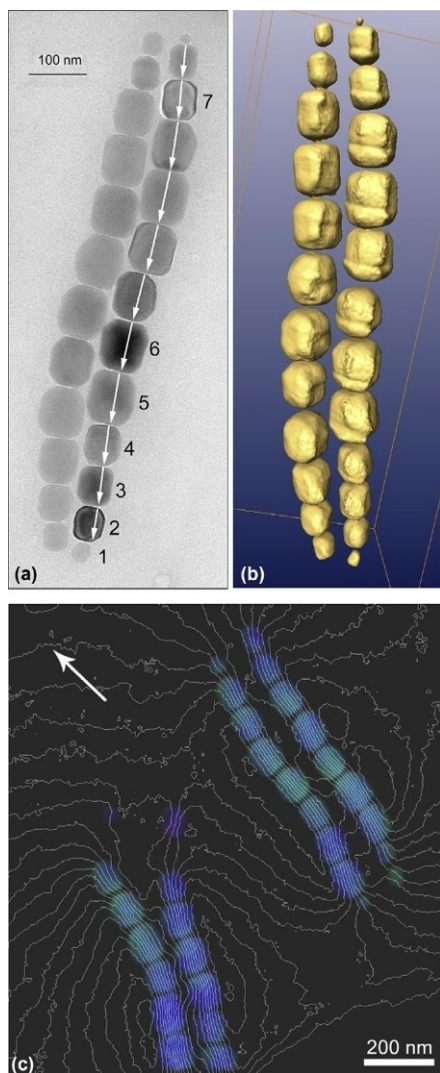


Figure 22 (a) Bright-field TEM image of a double chain of magnetite magnetosomes, acquired at 400 kV using a JEOL 4000EX TEM (image courtesy of M. Pósfai). The white arrows are approximately parallel to [111] in each crystal. (b) Electron tomographic reconstruction of the 3-D morphology of the double magnetosome chain shown in (a) (image courtesy of R. Chong). (c) Magnetic phase contours measured using electron holography from two pairs of bacterial magnetite chains at 293 K, after magnetizing the sample parallel and antiparallel to the direction of the white arrow. Parts (a) and (c) adapted from Simpson ET, Kasama T, Pósfai M, et al. (2005) Magnetic induction mapping of magnetite chains in magnetotactic bacteria at room temperature and close to the Verwey transition using electron holography. *Journal of Physics: Conference Series* 17: 108–121, with permission.

be possible, thereby optimizing the overall magnetic moment of the chain.

In **Figure 22**, strong magnetostatic interactions between crystals, combined with their high degree of alignment, result in uniform magnetic phase contours that are constrained tightly along the chain axis. In this case, the magnetic induction of the chain can be quantified by assuming that it has approximately a cylindrical geometry (eqn [22]), yielding a value for $B_{\perp}$ of 0.62 T for one of the central crystals. This

value is close to that predicted for magnetite ($B_0 = 0.6$ T), suggesting that the crystals are magnetized parallel to their length and to the chain axis. Interacting chains of closely spaced crystals are always magnetized along the chain axis, thus providing a reliable magnetic moment for magnetotaxis. This is confirmed by hysteresis (Pan et al., 2005; see **Section 2.24.5**) and remanence experiments (Hanzlik et al., 2002) on magnetotactic bacteria, which demonstrate that chains of magnetosomes act like a single elongated particle (with uniaxial anisotropy) and switch as a single unit.

When the alignment of crystals in a chain is less than perfect, it is possible to produce a nonuniform magnetization state by the application of a suitably oriented magnetic field (**Figure 23**). **Figure 23(a)** illustrates the magnetization state of two double chains of magnetite crystals (from the same bacterial cell) after the application of a magnetic field with an in-plane component of 1 T parallel to the chain axes. Despite the imperfect alignment of the crystals in the upper double chain, all four chains are magnetized along their length. Some flux divergence is evident where large gaps occur between crystals in the upper double chain, indicating that magnetostatic interactions are weakened slightly at these positions. **Figure 23(b)** illustrates the magnetization state after application of a similar magnetic field perpendicular to the chain axes. Although three out of the four chains are unaffected by the change in the applied field direction, the uppermost chain is split into two halves, each of which has a small component of its magnetization in the direction of the applied field. The two crystals in the center of the chain are now arranged in an energetically unfavorable opposing configuration, and the magnetization of one of the crystals is deflected so that it points at an angle of $\sim 60^\circ$ to the chain axis.

Figure 24 shows magnetic induction maps that have been acquired from a similar pair of magnetite chains both at room temperature and at 116 K (close to the Verwey transition). Whereas the contours are highly parallel to each other and to the chain axes at room temperature (**Figure 24(a)**), their direction is far more variable and irregular at low temperature (**Figure 24(b)**). This behavior is most pronounced in some crystals in **Figure 24(b)** that show S-shaped magnetic configurations. As mentioned earlier, in magnetite, the change in structure from cubic to monoclinic at the Verwey transition is associated with a change in easy axis from $\langle 111 \rangle$ to $\langle 100 \rangle$. Although particle interactions and shape anisotropy result in the preservation of the overall magnetic induction direction in **Figure 24(b)** along the chain axis at low temperature, it is likely that the undulation of the contours along the chain axes results from a competition between the effects of magnetocrystalline anisotropy, shape anisotropy, and magnetostatic interactions, which are only mutually favorable at room temperature.

2.24.3.3.3 Electron holography of 2-D magnetite nanoparticle arrays

In contrast to the sizes of crystals in magnetotactic bacteria, the grain sizes of primary magnetic minerals in most igneous and metamorphic rocks exceed the MD threshold. Such rocks are less likely to maintain strong and stable NRM over geologic times than those containing SD grains. It has long been proposed, however, that solid-state processes such as subsolvus

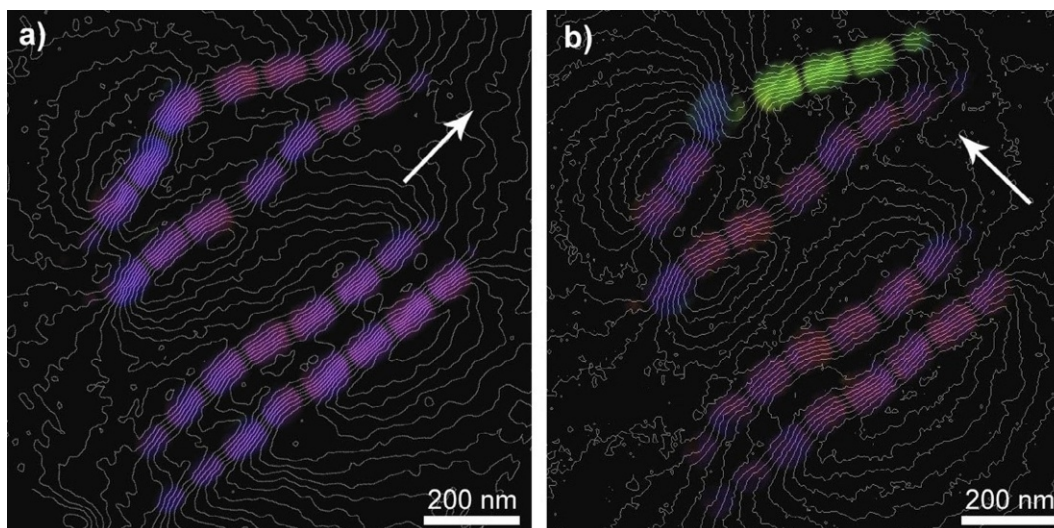


Figure 23 Illustration of the effect of changing the applied magnetic field direction on magnetic induction maps measured from two pairs of magnetite chains at 293 K. The applied field directions are indicated using white arrows. In (a), the chains are magnetized in the same direction. In (b), the topmost chain is partially magnetized antiparallel to the other chains in the figure. Adapted from Simpson ET, Kasama T, Pósfai M, et al. (2005) Magnetic induction mapping of magnetite chains in magnetotactic bacteria at room temperature and close to the Verwey transition using electron holography. *Journal of Physics: Conference Series* 17: 108–121, with permission.

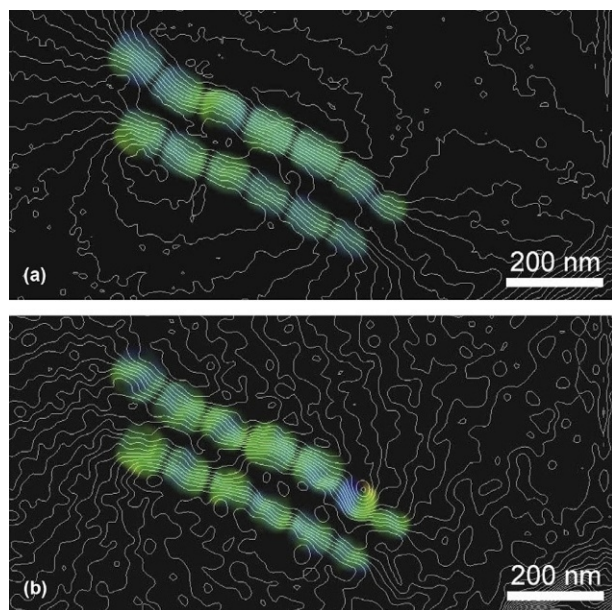


Figure 24 Magnetic induction maps acquired from two pairs of bacterial magnetite chains at (a) 293 K and (b) 116 K. In the room-temperature holograms, the contours are parallel to each other within the crystals and only deviate as a result of their morphologies and positions. At 116 K, this regularity is less evident. The field lines undulate to a greater degree within the crystals, as well as at kinks in the chains. The small vortex in the lower chain in (b) is likely to be an artifact resulting from diffraction contrast in this crystal. Adapted from Simpson ET, Kasama T, Pósfai M, et al. (2005) Magnetic induction mapping of magnetite chains in magnetotactic bacteria at room temperature and close to the Verwey transition using electron holography. *Journal of Physics: Conference Series* 17: 108–121, with permission.

exsolution can transform an MD grain into a collection of SD grains, thus increasing the stability of the NRM (Davis and Evans, 1976). This transformation is brought about by the formation of intersecting PM exsolution lamellae, which divide the host grain into a 3-D array of isolated magnetic regions that have SD-PSD sizes.

An excellent example of this phenomenon occurs in the magnetite-ulvöspinel ($\text{Fe}_3\text{O}_4\text{--Fe}_2\text{TiO}_4$) solid solution (Davis and Evans, 1976; Price, 1980, 1981). This system forms a complete solid solution at temperatures above $\sim 450^\circ\text{C}$ but unmixes at lower temperatures (Ghiorso, 1997). Intermediate bulk compositions exsolve during slow cooling to yield an intergrowth of SD- or PSD-sized magnetite-rich blocks that are separated by nonmagnetic ulvöspinel-rich lamellae. Figure 25(a) illustrates the typical microstructure observed in a natural sample of exsolved titanomagnetite (Harrison et al., 2002). This image is a composite chemical map, obtained using energy-filtered TEM imaging, showing the distribution of Fe in blue (magnetite) and Ti in red (ulvöspinel). Ulvöspinel lamellae form preferentially parallel to [100] planes of the cubic magnetite host lattice. In TEM sections that are oriented parallel to [100], this symmetry generates a rectangular array of cuboidal magnetite blocks. Profiles of the Fe and Ti distribution along the line marked C (Figure 25(b)) demonstrate that the blocks are essentially free of Ti, that is, they are nearly pure magnetite.

Harrison et al. (2002) used electron holography to determine the magnetic remanence states of region B in Figure 25(a). The magnetite blocks were found to be primarily in SD states (Figure 26). The dimensions of the blocks, which are plotted in Figure 21 for reference, indicate that the vast majority would display SV states at remanence if they were isolated and at equilibrium. Micromagnetic simulations of isolated cuboidal particles (Section 2.24.4) indicate that SD states can exist in

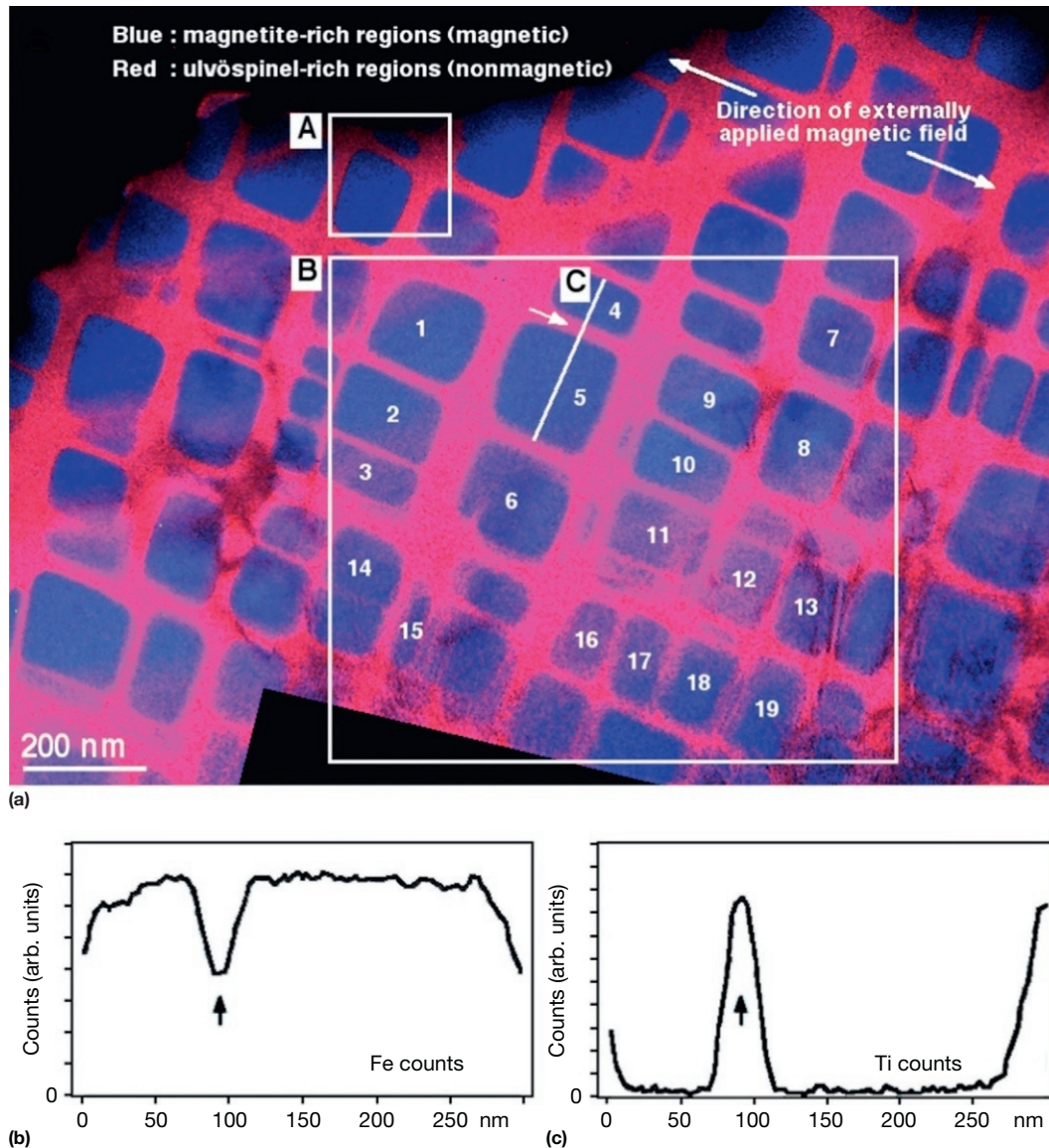


Figure 25 (a) Chemical map of a titanomagnetite sample, acquired by using electron spectroscopic imaging (Harrison et al., 2002). Blue and red correspond to Fe and Ti concentrations, respectively. The blue regions are magnetic and are rich in magnetite (Fe_3O_4), whereas the red regions are nonmagnetic and rich in ulvöspinel (Fe_2TiO_4). The numbers refer to individual magnetite-rich blocks, which are discussed in the text. (b) and (c) Line profiles obtained from the Fe and Ti chemical maps, respectively, along the line marked C in (a). The short arrows mark the same point in the three pictures.

metastable form up to a certain size above the equilibrium SD–SV threshold (Fabian et al., 1996; Williams and Wright, 1998; Witt et al., 2005). The majority of the blocks in Figure 26 fall within the limits of metastability for SD states calculated by Witt et al. (2005). It appears that the presence of magnetostatic interactions favors the adoption of metastable SD states over equilibrium SV states. This behavior results from the fact that the demagnetizing energy – which destabilizes the SD state with respect to the vortex state in isolated particles – is reduced greatly in an array of strongly interacting SD particles.

Transitions between different magnetic states in an individual block can be seen in Figure 26. For example, block 8 (labeled in Figure 25(a)) in Figure 26(e) is magnetized NNW (North North West; blue), whereas in Figure 26(f), it is

magnetized SSE (South South East; yellow). It contains an off-centered vortex in Figure 26(b), suggesting that magnetization reversal in this block may occur via the formation, displacement, and subsequent annihilation of a vortex (Dumas et al., 2007; Enkin and Williams, 1994; Guslienko et al., 2001; Pike and Fernandez, 1999), rather than by the coherent rotation of the SD moment.

Several blocks are observed to act collectively to form magnetic ‘superstates’ that would normally be observed in a single, larger magnetized region. One example is where two or more blocks interact to form a SV superstate. Two-, three-, and five-block vortex superstates are visible in Figure 26 (e.g., blocks 1 and 2 in Figure 26(g) and blocks 1, 2, 3, 5, and 6 in Figure 26(e)). A similar superstate involving three elongated

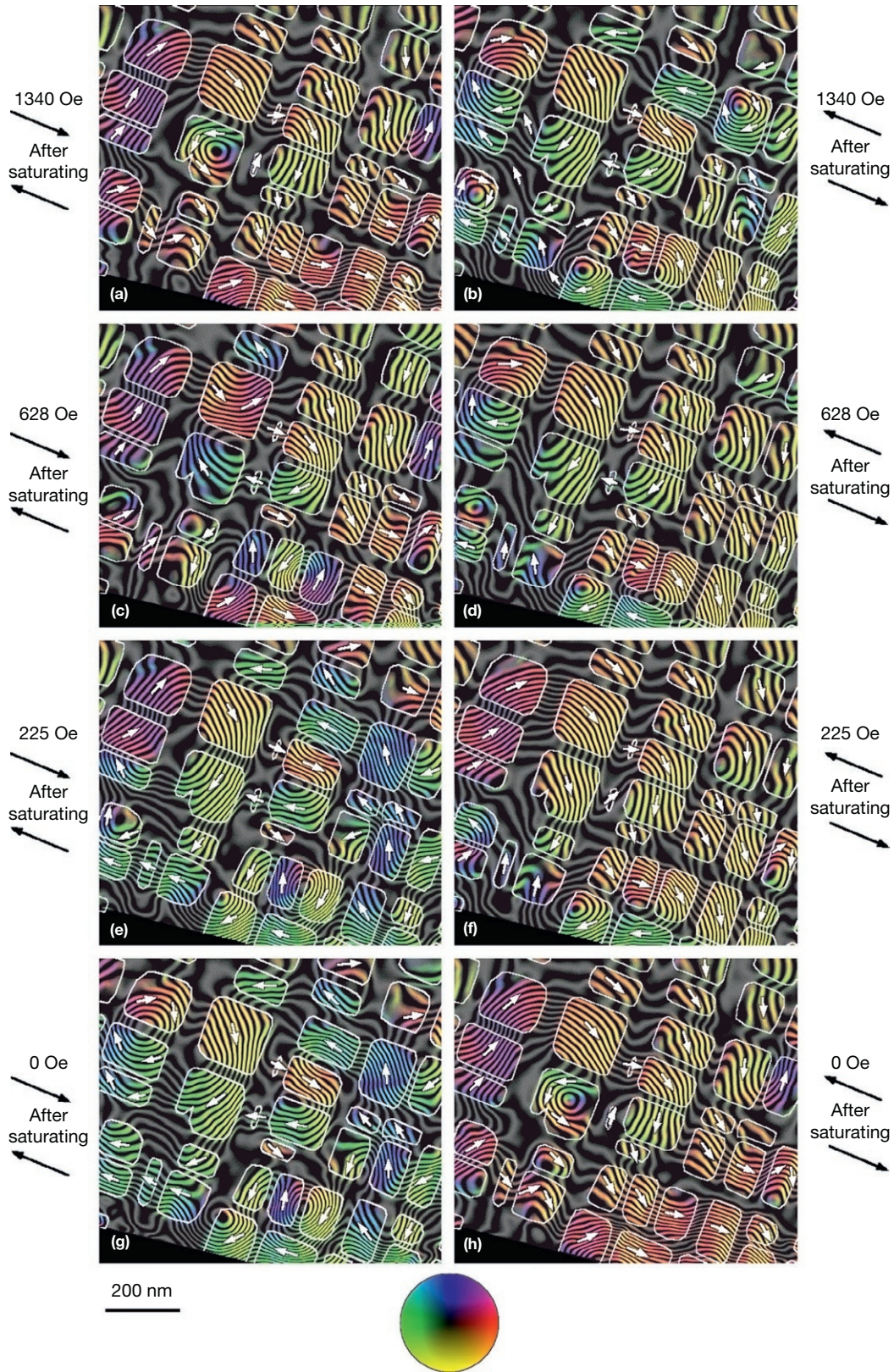


Figure 26 Magnetic microstructure of region B in [Figure 25\(a\)](#) measured by using electron holography ([Harrison et al., 2002](#)). Each image corresponds to a different magnetic remanent state, acquired with the sample in field-free conditions. The outlines of the magnetite-rich regions are marked in white, while the direction of the measured magnetic induction is indicated both using arrows and according to the color wheel shown at the bottom. Images (a), (c), (e), and (g) were obtained after applying a large field toward the top left of each picture and then the indicated field toward the bottom right, after which the external magnetic field was removed for hologram acquisition. Images (b), (d), (f), and (h) were obtained after applying identical fields in the opposite directions.

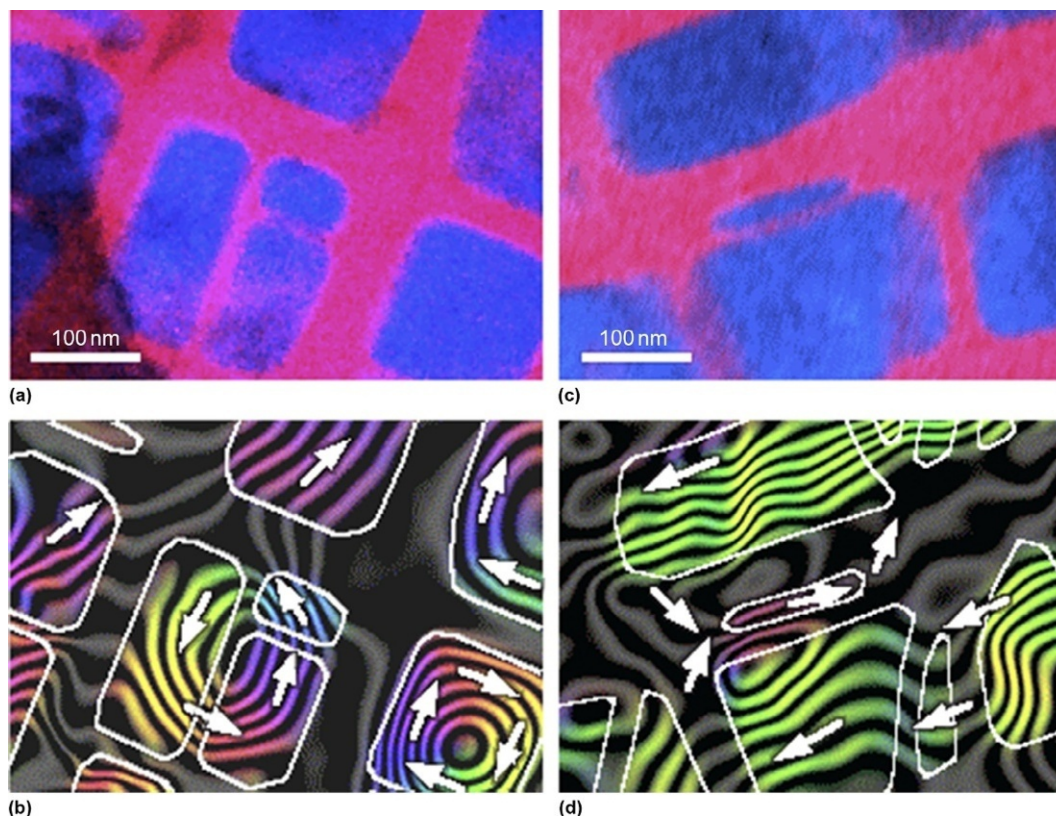


Figure 27 (a and c) Chemical maps (blue Fe and red Ti) from two regions not shown in Figure 25. (b and d) The corresponding magnetic microstructures, in the same format as Figure 26: (b) three adjacent magnetite-rich regions combining to form a single vortex and (d) a small region that is magnetically antiparallel to its larger neighbors.

blocks is shown in Figure 27(a) and 27(b) and schematically in Figure 28(a). The absence of closely spaced contours between the superstate and the adjacent SV in Figure 27(b) shows that stray interaction fields are eliminated in the intervening ulvöspinel. Flux closure is achieved with considerably less curvature of magnetization within the three-component assembly than is required in the adjacent conventional vortex, reducing the exchange energy penalty associated with the nonuniform magnetization configuration (Evans et al., 2006).

A second example of collective behavior involves the interaction of a chain of blocks to form an SD superstate that is magnetized parallel to the chain axis but perpendicular to the easy axes of the individual blocks. This behavior is illustrated schematically in Figure 28(b) and can be found in several places in Figure 26 (e.g., blocks 16, 17, and 18 in Figure 26(a), 26(b), 26(d), 26(f), and 26(h)). An extreme example of this behavior is shown in Figure 29, which shows saturation isothermal remanent states in an exsolved titanomagnetite inclusion within clinopyroxene (Feinberg et al., 2004, 2005). These states were recorded after tilting the sample by angles of $\pm 30^\circ$ and applying a 2 T vertical field (Figure 16). The in-plane component of the field was parallel to the elongation direction of the central blocks. Nevertheless, strong interactions between the blocks (which are separated by ~ 15 nm of ulvöspinel) constrain the remanence to lie almost perpendicular to the elongation direction of the individual blocks and to the applied field direction. The expected

remanent state of such a system might have been expected to involve adjacent blocks being magnetized in an alternating manner along their elongation directions, as is seen in blocks 16, 17, and 18 and blocks 9, 10, and 11 in Figure 26(c), 26(e), and 26(g) and shown schematically in Figure 28(c). It should be noted at this point that the role of stress-induced anisotropy has not been accounted for, and this may yet turn out to play a significant role in determining the magnetization directions in such intergrowths.

A further example of magnetostatic interactions between blocks is shown in Figure 27(d). The two largest blocks (colored green) are both magnetized in the same direction. The small block between them (colored red) is magnetized in the opposite direction, apparently because it follows the flux return paths of its larger neighbors.

2.24.3.3.4 Exchange interactions across antiphase boundaries in ilmenite–hematite

Harrison et al. (2005) used electron holography to study the nature of the exchange coupling at APBs in ilmenite–hematite. A sample of ilm70 was synthesized from the oxides under controlled oxygen fugacity at 1573 K, quenched through the cation-ordering phase transition, and annealed for 10 h at 1023 K. Representative magnetic induction maps are shown in Figure 30(a)–30(c). Each figure, which is derived from the gradient of the magnetic contribution to the recorded phase shift, shows a magnetic remanent state obtained at a different

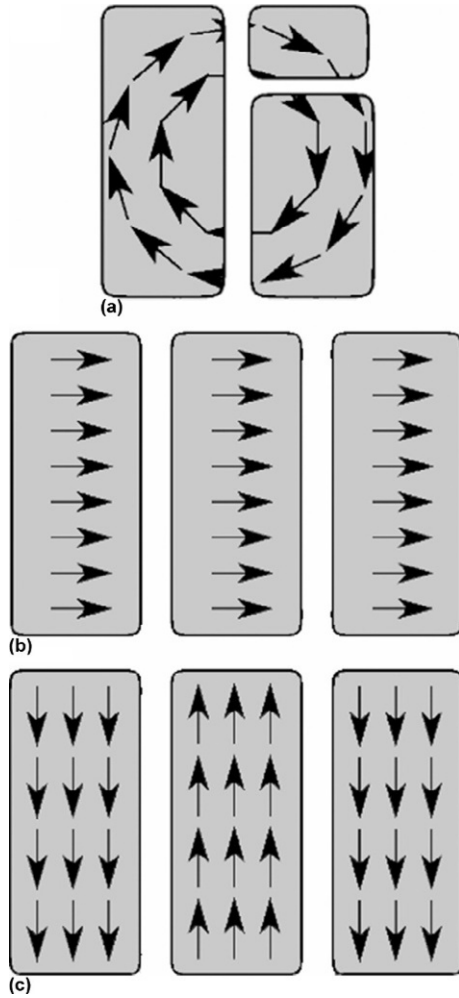


Figure 28 Schematic diagrams showing some of the possible magnetization states of three closely spaced regions of magnetic material.

stage of the switching process. The direction and magnitude of the in-plane magnetic flux are defined by the hue and intensity of the color, respectively.

The magnetization is constrained by shape and magnetocrystalline anisotropy to lie either parallel or antiparallel to the intersection of the specimen plane with the [001] crystallographic plane (indicated by the double black arrow in Figure 30). As a result, regions with strong in-plane magnetization appear either blue or green. Regions that have no in-plane magnetization appear as dark bands. Analysis (see Figure 31 in the succeeding text) shows that the dark bands in Figure 30 are associated with three distinct types of magnetic wall (Robinson et al., 2012, 2014). A fingerlike region of reversed magnetization (labeled '1' in Figure 30(a)) enlarges by the movement of its left-hand boundary as the applied field is increased (Figure 30(b)). This left-hand boundary is a conventional free-standing 180° Bloch wall. In contrast, in regions where a 180° reversal in magnetization direction coincides exactly with the position of an APB (e.g., at regions labeled '2'), the reversal results from negative exchange coupling across the APB, as predicted by Monte Carlo simulations (Figure 11).

This type of boundary is referred to as a 180° 'chemical' wall and occurs without any out-of-plane rotation of the magnetic moments. A third type of magnetic wall appears as thick dark bands, which are also coincident with the positions of APBs (e.g., at regions labeled '3'). Such walls form when the negative exchange coupling between adjacent APDs is overcome at sufficiently large fields, forcing the magnetization direction on either side to point in the same direction. These walls are referred to as 0° walls.

For a 180° Bloch wall, the in-plane component of the magnetic induction is generally described by an expression of the form

$$B_{\perp}(x) = B_0 \tanh\left(\frac{x}{w}\right) \quad [27]$$

where B_0 is the saturation induction and $2w$ is the wall width. By substituting eqn [27] into eqn [13], the magnetic phase profile across a 180° Bloch wall (assuming a constant thickness, t) is

$$\phi(x) = B_0 t w \ln\left(\cosh\left(\frac{x}{w}\right)\right) \quad [28]$$

Equation [28] provides an excellent fit to the phase profile of a 180° Bloch wall for $2w = 19$ nm (Figure 31(a)). In contrast, the phase profile on either side of a 180° chemical wall is nonlinear (see succeeding text), and the reversal in the slope of the phase profile at the center of the wall occurs much more abruptly (Figure 31(b)). A fit to the central portion of this wall yields $2w = 7$ nm (dashed line in Figure 31(b)). This value is close to the resolution limit of the measurements and provides an upper limit for the width of the chemical wall. A 0° wall can be considered as the superposition of a 180° Bloch wall and a 180° chemical wall. Assuming that both types of wall can be described by eqn [27] with the same value of w , the in-plane component of magnetic induction is of the form

$$B_{\perp}(x) = B_0 \tanh^2\left(\frac{x}{w}\right) \quad [29]$$

By substituting eqn [29] into eqn [13], the magnetic phase profile across a 0° wall is

$$\phi(x) = B_0 t \left[x - 10 \tanh\left(\frac{x}{w}\right) \right] \quad [30]$$

Equation [30] provides an excellent fit to the phase profile of a 0° Bloch wall (Figure 31(c)). An average of 13 measurements yielded $2w = (50 \pm 14)$ nm for 0° walls. Previous studies demonstrated that SR-TRM was observed only when APDs were below 80–100 nm in size (Nord and Lawson, 1989, 1992). This limit is imposed by the formation of 0° walls, which allow negative exchange coupling between adjacent domains to be overcome when the APDs are much larger than 50 nm in size. A detailed exploration of the interaction between chemical and magnetic boundaries, and its role in the acquisition of SR-TRM in ilmenite-hematite, is given by Fabian et al. (2011) and Robinson et al. (2012, 2013).

2.24.4 Magnetism at the Micrometer Length Scale

Due to the large number of atoms and spins involved, atomistic simulations, which describe the discrete arrangement of

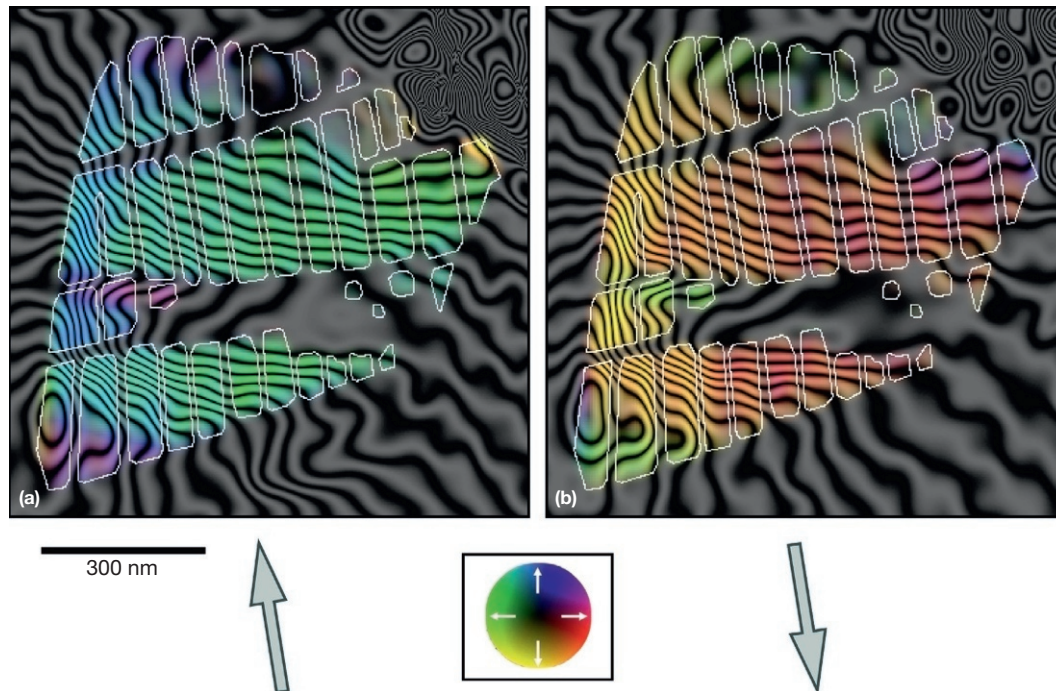


Figure 29 Magnetic induction maps of a titanomagnetite inclusion within pyroxene (Feinberg et al., 2004, 2005). The inclusion is an intergrowth of elongated magnetite blocks (outlined in white) separated by lamellae of ulvöspinel. (a and b) Correspond to saturation remanent states obtained after tilting the sample to $\pm 30^\circ$ in the vertical 2 T of the TEM objective lens, such that the in-plane component of the applied field was directed along the gray arrows. Note that the magnetic microstructures in (a) and (b) are the exact reverse of each other, allowing the mean inner potential to be determined using the method described in Section 2.24.3.1.5.

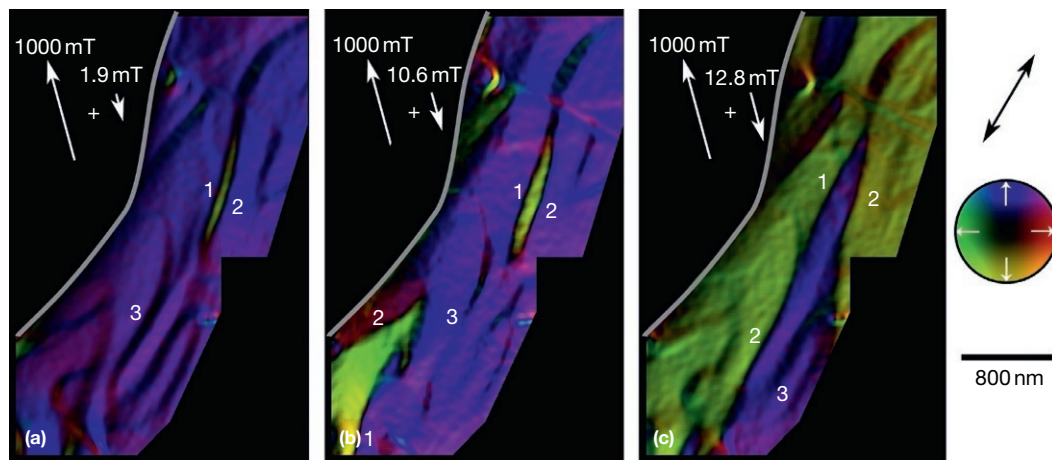


Figure 30 Magnetic microstructure of ilm70 containing several APDs (Harrison et al., 2005). The sample edge is indicated by the gray line. Prior to each measurement, the sample was exposed to a saturating field with an in-plane–out-of-plane component of $+1000/+1732$ mT, followed by a smaller field with an in-plane–out-of-plane component of (a) $-1.9/+3.3$ mT, (b) $-10.6/+18.4$ mT, and (c) $-12.8/+22.2$ mT. White arrows indicate the direction of the in-plane component of the applied field. The hue and intensity of the color indicate the direction and magnitude of the in-plane component of the magnetic flux in the sample in field-free conditions, as defined by the color wheel on the right. The blue-purple and green-yellow colors correspond to equal and opposite in-plane magnetizations in the direction indicated by the black double arrow. The dark bands indicate regions with weak in-plane magnetization (magnetic domain walls). Dark bands that separate regions of blue and green colors correspond to 180° magnetic and chemical walls (e.g., at regions labeled ‘1’ and ‘2,’ respectively). Dark bands that are surrounded by regions of the same color correspond to 0° magnetic walls (e.g., at regions labeled ‘3’).

atoms and spins on a crystalline lattice, are currently unsuitable for systems larger than ~ 10 nm (Section 2.24.2). The magnetization states of larger particles (or collections of particles) are more efficiently described using micromagnetic simulations (Brown, 1963). Micromagnetics is the study of

magnetization at the nanometer to micrometer length scale (i.e., a length scale that is much larger than that of the crystalline lattice but smaller than that of a magnetic domain). Micromagnetic models treat magnetization as a classical, continuous vector field in space. The energy of the system is described by a

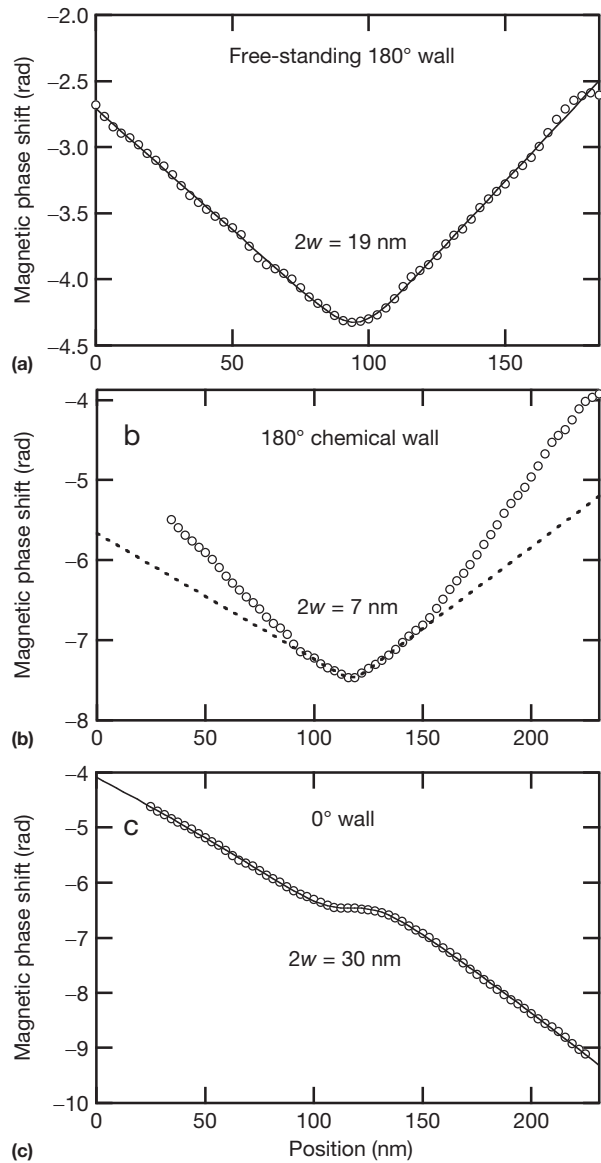


Figure 31 Profiles of the holographic phase shift, ϕ , across three distinct types of magnetic domain wall in ilm70 (Harrison et al., 2005). The gradient of each profile is proportional to the in-plane component of the magnetic flux (eqn [15]). (a) A free-standing 180° Bloch wall. The solid line is a least squares fit to the observed profile, obtained by using eqn [28] and yielding a wall width of 19 nm. (b) A 180° 'chemical' wall that is coincident with an APB. The dashed line is a fit to the central portion of the wall, obtained by using eqn [28] and yielding a wall width of 7 nm. (c) A 0° magnetic wall that is coincident with the same APB as in (b). The slope of the phase profile has the same sign on either side of the wall, indicating that the direction of magnetization is the same. The solid line is a fit to the profile, obtained using eqn [30] and yielding a wall width of 30 nm.

number of macroscopic constants, whose values can be derived from their microscopic equivalents (eqn [2]). Micromagnetic simulations of magnetic minerals have progressed rapidly from 1-D (Moon, 1991; Moon and Merrill, 1984, 1985) to 2-D (Newell et al., 1993; Xu et al., 1994) to 3-D (Fabian et al., 1996; Schabes and Bertram, 1988a,b; Williams and Dunlop,

1989, 1990; Williams and Wright, 1998; Wright et al., 1997) models of homogeneous isolated single crystals with simple geometric shapes. The recent application of finite element-boundary element methods (FEMs-BEMs) to micromagnetic simulations now allows the simulation of heterogeneous, polycrystalline systems that have complex and realistic morphologies (Chang et al., 2012; Fidler and Schrefl, 2000; Williams et al., 2006, 2010, 2011). In addition, substantial progress is being made in the application of micromagnetic simulations to the study of magnetostatic and exchange interactions between arrays of closely spaced magnetic particles (Carvallo et al., 2003; Evans et al., 2006; Muxworthy and Williams, 2005, 2006; Muxworthy et al., 2003a, 2004) and to the application of micromagnetics to the study of the interaction between magnetic domains and ferroelastic twin domains below the Verwey transition in magnetite (Bryson et al., 2012; Kasama et al., 2010, 2012).

2.24.4.1 Theory

We begin by summarizing the basic principles of micromagnetics, as applied to rock magnetic problems. For detailed reviews of the technical aspects of micromagnetic simulations, the reader is referred to Brown (1963), Wright et al. (1997), Fabian et al. (1996), and Fidler and Schrefl (2000).

2.24.4.1.1 The micromagnetic energy

Micromagnetism is a continuum approximation, in which the magnetization of a particle is taken to be a continuous function of position (c.f. eqn [25]):

$$\mathbf{m}(\mathbf{r}) = \frac{\mathbf{M}(\mathbf{r})}{M_s} = \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} = \begin{pmatrix} \cos(\phi)\sin(\theta) \\ \sin(\phi)\sin(\theta) \\ \cos(\theta) \end{pmatrix} \quad [31]$$

where $\mathbf{m}$ is a unit vector parallel to the magnetization direction $\mathbf{M}$ at position $\mathbf{r}$ and M_s is the saturation magnetization. The direction of $\mathbf{m}$ is defined either in terms of direction cosines α , β , and γ or in terms of the polar coordinates ϕ and θ . $\mathbf{M}$ represents the local average of many thousands of individual spins.

Minimization of the microscopic exchange energy (eqn [1]) requires $\mathbf{m}$ to be uniform throughout a grain. Deviations from uniform magnetization at the macroscopic length scale impose deviations on the angles between adjacent spins at the atomic scale. On the assumption that these angular deviations are small, the macroscopic exchange energy can be expressed in the form of a truncated Taylor expansion of eqn [1]:

$$E_{\text{ex}} = A \int_V (\nabla \mathbf{m})^2 dV \quad [32]$$

where the exchange constant A is related to the atomistic exchange integrals and V is the volume of the particle. The exchange energy is positive wherever gradients in the macroscopic magnetization occur (e.g., within domain walls) and zero wherever the magnetization is uniform (e.g., within domains).

Since the angular relationship between the atomic spins and the net magnetization is fixed, the macroscopic expression for the magnetocrystalline anisotropy energy is equivalent to that in eqn [2]. For uniaxial anisotropy, this expression is

$$E_a = - \int_V K(\mathbf{m} \cdot \mathbf{e})^2 dV \quad [33]$$

while for cubic magnetocrystalline anisotropy, the expression is

$$E_a = - \int_V [K_1(\alpha^2\beta^2 + \beta^2\gamma^2 + \gamma^2\alpha^2) + K_2\alpha^2\beta^2\gamma^2] dV \quad [34]$$

Similarly, the macroscopic expression for the magnetostatic energy is equivalent to that in eqn [2]:

$$E_h = -\mu_0 M_S \int_V \mathbf{H}_{\text{ext}} \cdot \mathbf{m} dV \quad [35]$$

where $\mathbf{H}_{\text{ext}}$ is the applied magnetic field.

Calculation of the demagnetizing energy is the most challenging and computationally intensive part of any micromagnetic simulation. A macroscopic expression for the demagnetizing energy (eqn [3]) can be formulated in terms of the demagnetizing field, $\mathbf{H}_d(\mathbf{r})$, which is the sum of the magnetic fields at position $\mathbf{r}$ created by all of the magnetic moments in the particle:

$$E_d = -\frac{1}{2}\mu_0 M_S \int_V \mathbf{m} \cdot \mathbf{H}_d dV \quad [36]$$

A general method for calculating $\mathbf{H}_d$ follows from Maxwell's equations in a current-free region with static electric and magnetic fields:

$$\nabla \times \mathbf{H} = 0 \quad [37]$$

$$\nabla \cdot \mathbf{B} = \mu_0 \nabla \cdot (\mathbf{H} + \mathbf{M}) = 0 \quad [38]$$

From eqn [37], it follows that the magnetic field, $\mathbf{H} = \mathbf{H}_{\text{ext}} + \mathbf{H}_d$, can be described as the gradient of a magnetic scalar potential, ϕ :

$$\mathbf{H} = -\nabla\phi \quad [39]$$

By rearranging eqn [38], one obtains Poisson's equation:

$$\nabla^2 \phi = \nabla \cdot \mathbf{M} \quad [40]$$

Outside the particle, $\mathbf{M}$ is zero, and eqn [40] reduces to the Laplace equation:

$$\nabla^2 \phi = 0 \quad [41]$$

The general solution to eqn [40] is of the form

$$\phi(\mathbf{r}) = \frac{1}{4\pi} \left[\int_V \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} dV' + \int_S \frac{\sigma(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} dS' \right] \quad [42]$$

where $\rho(\mathbf{r}) = -\nabla \cdot \mathbf{M}$ is the density of magnetic volume charges due to nonzero divergence of the magnetization within the interior of the particle and $\sigma(\mathbf{r}) = \mathbf{M} \cdot \hat{\mathbf{n}}$ is the density of magnetic surface charges due to the component of magnetization normal to the particle surface ($\hat{\mathbf{n}}$).

The total energy of the system is the sum of exchange, anisotropy, magnetostatic, and demagnetizing energies:

$$E_{\text{tot}} = E_{\text{ex}} + E_a + E_h + E_d \quad [43]$$

Important energy terms that are missing from eqn [43] include the magnetoelastic energy arising from the stress fields surrounding dislocations and other lattice defects and the

magnetostrictive self-energy associated with the elastic strain of an inhomogeneously magnetized particle. For a mineral such as magnetite, magnetostriction can be neglected for particles that are smaller than $\sim 6 \mu\text{m}$ (Fabian and Heider, 1996). The inclusion of magnetostriction into micromagnetic models of titanomagnetite is discussed by Fabian and Heider (1996).

2.24.4.1.2 Discretization of the micromagnetic energy

Although micromagnetism is a continuum approach, numerical calculation and minimization of the total energy (eqn [43]) require discretization of the volume that describes the object of interest. The most common approach is to divide the object into a 3-D mesh of cubic elements. Each element is assigned a magnetization vector at its center (eqn [31]) and is assumed to be magnetized homogeneously. The elements must be large enough to average out the discrete effects of the crystalline lattice (i.e., they should be significantly larger than the unit cell size), yet small enough that the angular differences between the magnetization directions of adjacent cubes are smaller than $\sim 15^\circ$ (Williams and Wright, 1998). This upper limit is imposed by the use of a truncated Taylor expansion for the exchange energy (eqn [32]), which assumes that the gradient of the magnetization is small. Assuming that the magnetization varies most rapidly at domain walls (which have a width of $\sim 100 \text{ nm}$ wide in magnetite) and that approximately 4–10 elements are required over this distance to obtain an accurate value for the exchange energy, the maximum element size is of the order 10–25 nm. Larger element sizes can be used in cases where the magnetization remains fairly uniform and also if the primary interest is in examining the effects of magnetostatic interactions between particles rather than the magnetization states of individual particles (Muxworthy et al., 2003a). A minimum of two elements per exchange length, $l = \sqrt{A/K_d}$, where $K_d = \mu_0 M_S^2/2$ is usually recommended (Rave et al., 1998).

The exchange, anisotropy, and magnetostatic contributions to the total energy (eqn [43]) are functions of the local magnetization and its derivatives. After discretization of the particle volume, these terms are readily calculated using finite-difference (FD) methods (Wright et al., 1997). Calculating the demagnetizing energy, however, involves summing over contributions from all elements in the system. The assumption that each element is magnetized uniformly (i.e., $\nabla \cdot \mathbf{M} = 0$) eliminates the volume-charge contribution to the magnetic scalar potential (the first term in eqn [42]) and reduces the problem to summing the surface-charge contributions from the faces of each element. The calculation can be simplified further by transforming eqn [42] into a product of spatial terms (i.e., terms that depend only on the geometric relationship between pairs of elements) and angular terms (i.e., terms that depend on the direction of magnetization within each element). The demagnetizing energy can then be expressed in the form

$$E_d = \frac{\mu_0 M_S^2}{8\pi} \sum_{l=1}^N \sum_{m=1}^N W_{l-m}^{\alpha\beta} \alpha_l \beta_m \quad [44]$$

where $W_{l-m}^{\alpha\beta}$ are spatial coefficients (evaluated using the method of Rhodes and Rowlands, 1954), α and β are angular terms corresponding to the charges of different faces of each

element, and N is the number of elements (Wright et al., 1997). The spatial terms can be evaluated once at the start of the simulation and stored in a lookup table. The summation can be accelerated greatly using FFT methods, whereby eqn [44] is rewritten as a convolution and summed in frequency space (Fabian et al., 1996; Wright et al., 1997).

The total energy must be minimized in order to obtain the equilibrium magnetization state of the object. Dynamic approaches make use of the LLG equation of motion (eqn [5]) and are particularly suitable for the study of magnetization reversal processes. Alternatively, conjugate gradient (Fabian et al., 1996; Wright et al., 1997), Monte Carlo (Kirschner et al., 2005), or simulated annealing (Thomson et al., 1994; Winklhofer et al., 1997) methods may be used. Whereas simulated annealing and Monte Carlo methods are typically used to find the magnetic domain state that corresponds to the absolute energy minimum (AEM) of the object, the use of LLG and conjugate gradient techniques typically results in the determination of magnetic domain states that represent local energy minima (LEM). The LEM state that is obtained depends on the initial state of the particle. Simulations typically start with the smallest particle size, which is initialized with a uniform magnetization state in a chosen direction. The final magnetic structure obtained for that particle size serves as the initial guess for the next, slightly larger, particle size. In this way, systematic changes in domain structure as a function of particle size and shape can be determined.

2.24.4.1.3 Finite element discretization

Most naturally occurring magnetic particles have irregular morphologies. Discretization using a regular array of cubes provides a poor description of noncuboidal grain shapes (Figure 32). Curved boundaries are approximated simply by assigning a value of $M=0$ to certain elements of the regular cubic array ('cell blanking'). The FD discretization of a sphere shown in Figure 32(a) has a highly stepped surface, which may result in magnetostatic artifacts that can drastically alter its predicted magnetic domain structure, behavior, and stability. Improvements to this approach can be made by assigning values of M according to the volume fraction of each element that is enclosed by the true particle volume (Witt et al., 2005). In this way, elements that

occur entirely within the particle have $M=M_s$, elements entirely outside the particle have $M=0$, and those at the boundary have $0 < M < M_s$. State-of-the-art micromagnetic simulations involve the use of FEMs to simulate magnetic domain structure in complex geometries (Fidler and Schrefl, 2000). Efficient discretization is then carried out using a combination of triangles, squares, and rectangles (in two dimensions) or tetrahedra, cubes, and hexahedra (in three dimensions). An FEM discretization using 60 tetrahedral elements (Figure 32(b)) provides a much better representation of a sphere than the FD discretization using 343 cubic elements (Figure 32(a)). FE models reduce magnetostatic artifacts that originate on grain surfaces drastically. In order to determine the demagnetizing energy when using FEMs, each node of the FE mesh is associated with a value of the magnetic scalar potential. Values of ϕ are determined by solving Poisson's equation (eqn [40]) inside the particle and Laplace equation (eqn [41]) outside the particle, subject to the following boundary conditions (Fidler and Schrefl, 2000):

$$\phi_{\text{int}} = \phi_{\text{ext}} \quad [45]$$

$$(\nabla \phi_{\text{int}} - \nabla \phi_{\text{ext}}) \cdot \hat{n} = M \cdot \hat{n} \quad [46]$$

Because FEMs do not require the use of a regular periodic array of nodes, it is possible to adapt the mesh to better suit a given pattern of nonuniform magnetization. For example, it is more efficient to have a high density of nodes in regions where the magnetization varies rapidly and a low density of nodes in regions where the magnetization remains uniform. Adaptive mesh algorithms actively modify the FE mesh in response to the changing magnetization state of the system and guarantee that accurate solutions are obtained near magnetic inhomogeneities or domain walls while keeping the number of elements to a minimum (Fidler and Schrefl, 2000; Scholz et al., 1999).

2.24.4.2 Applications of Micromagnetic Simulations

2.24.4.2.1 Equilibrium domain states in isolated magnetite particles

High-resolution micromagnetic studies of isolated cuboidal magnetite particles in the size range 10–4 μm have been performed by Williams and Wright (1998), Fabian et al. (1996),

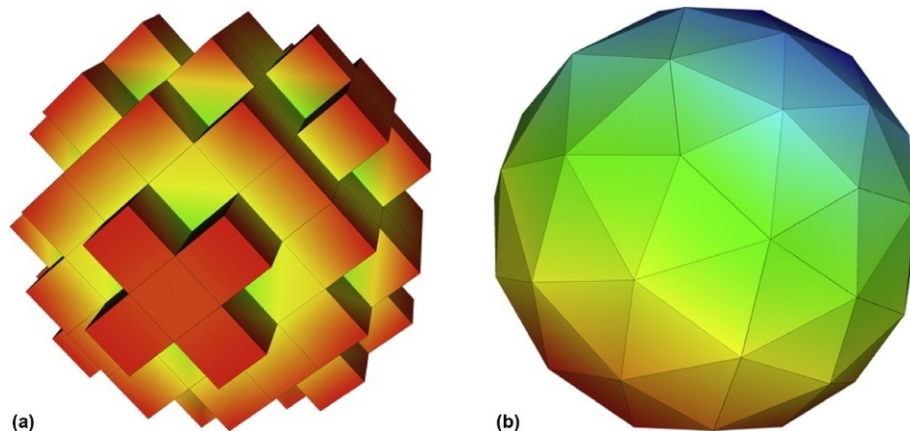


Figure 32 Discretization of a spherical particle using (a) regular array of 343 cubic elements (including blanks) and (b) finite element mesh of 60 tetrahedra (image courtesy of W. Williams).

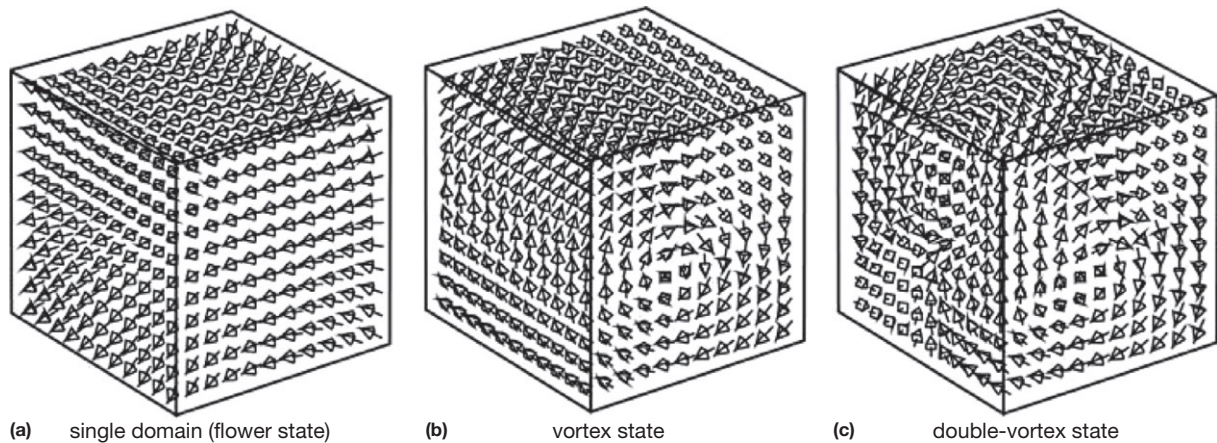


Figure 33 Calculated domain states occurring in cubic grains of magnetite at room temperature for a grain with edge length of 120 nm (a) single-domain (flower) state, (b) single-vortex state, and (c) double-vortex state. The [001] axis aligns with the z-axis of the cube. It was necessary to constrain **Figure 32(c)** for a 120 nm cube. Reproduced from Muxworthy AR, Dunlop DJ, and Williams W (2003) High-temperature magnetic stability of small magnetite particles. *Journal of Geophysical Research* 108: 2281, with permission.

Witt et al. (2005), and Fukuma and Dunlop (2006) using FFT-accelerated FD methods combined with conjugate gradient energy minimization (Wright et al., 1997). The domain states that are found to be stable in cubic particles in the size range 10–400 nm are (i) a uniformly magnetized SD state, (ii) a flower (F) state (**Figure 33(a)**), and (iii) an SV state (**Figure 33(b)**). Fabian et al. (1996), Winklhofer et al. (1997), and Witt et al. (2005) demonstrated that a double-vortex state (**Figure 33(c)**) exists as an LEM state in cubes that are larger than 300 nm, although the appearance of this state appears to be sensitive to the precision used in the simulations. Both F and SV states reduce the component of magnetization normal to the particle surface, thereby reducing the demagnetizing energy (eqn [42]). Although F states are not magnetized uniformly, they still obey the Néel (1949) SD theory of thermoremanent and viscous remanent magnetization. For this reason, SD and F states are often referred to interchangeably.

The variation in the total micromagnetic energy of a magnetite cube with particle size is illustrated in **Figure 34** (Muxworthy et al., 2003b). The starting configuration was a 50 nm cube with uniform magnetization. This SD state relaxes to an F state, which is then used as the starting configuration for the next largest particle. The F state remains metastable up to a particle size of 96 nm. Above this critical size, it relaxes spontaneously to an SV state that has a much lower energy. If the SV state is studied as a function of gradually decreasing particle size, then its energy intersects that of the F state at a particle size of 64 nm. Hence, 64 and 96 nm correspond to the lower and upper limits for the sizes of isolated magnetite cubes that can support metastable F states. Above a particle size of 64 nm, the SV state represents the stable AEM state of the particle. The F state can exist, however, as a metastable LEM state up to a particle size of 96 nm. Direct experimental observation of metallic Fe nanoparticles that display both stable SV and metastable F states have been reported by Lappe et al. (2011) using electron holography. On decreasing the particle size, the SV to F state transition is continuous, corresponding to a gradual ‘unwinding’ of the vortex (Williams and Wright, 1998). There is close agreement between different micromagnetic studies regarding the lower limit of SV stability (64–70 nm) but significant variation regarding the upper limit

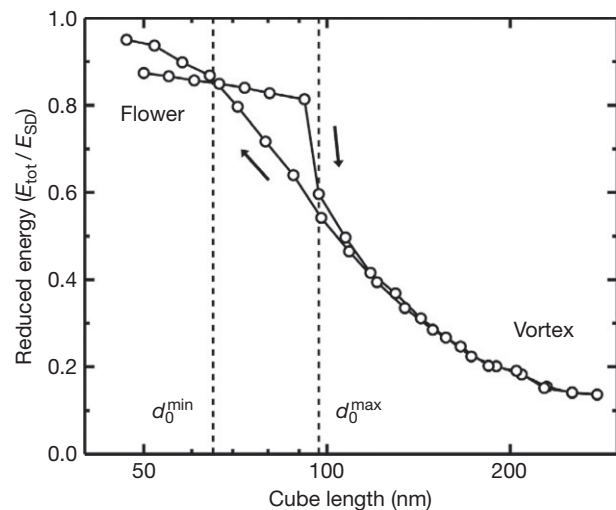


Figure 34 Calculated micromagnetic energy density of a magnetite cube as a function of edge length d for an initial SD configuration at room temperature (**Figure 32(a)**). The grain size was gradually increased until the SD structure collapsed to a vortex structure at $d_0^{\max} = 96$ nm. The size was then gradually decreased until a SD state formed at $d_0^{\min} = 64$ nm. Reproduced from Muxworthy AR, Dunlop DJ, and Williams W (2003) High-temperature magnetic stability of small magnetite particles. *Journal of Geophysical Research* 108: 2281, with permission.

(96–220 nm) (Fabian et al., 1996; Muxworthy et al., 2003b; Williams and Wright, 1998; Witt et al., 2005). The lower limit is defined strictly as the particle size at which the absolute energies of the two alternative states become equal, whereas the upper limit is determined by the disappearance of the energy barrier separating two states that have very different energies. The latter transition is sensitive to the precision of the calculation and the method used to determine the energy minimum and is therefore subject to more variation from study to study.

A gradual transition to classical MD states occurs for particle sizes in the range 1–4 μm . This transition, which is described in **Figure 35**, is characterized by (Williams and Wright, 1998) (i) an alignment of the near-surface magnetization parallel to the

particle surface; (ii) an alignment of the magnetization with the magnetocrystalline easy axes (or the projection of the easy axes on the particle surface); (iii) an increase in the fraction of the particle volume occupied by regions of uniform magnetization; (iv) a decrease in the size, together with a more domain wall-like appearance, of the nonuniformly magnetized regions; (v) tilting of vortex cores away from [001], allowing larger regions of magnetization to point along the magnetocrystalline easy axes; and (vi) vortex cores in larger particles becoming nucleation centers for domain walls.

The magnetic structures of noncuboidal particles have been investigated using a modified version of the cell-blanking technique by Witt et al. (2005) and by FE methods by Williams et al. (2006). Williams et al. (2006) demonstrated that noncuboidal particles can develop significant 'configurational anisotropy' as the F state adjusts itself to accommodate the grain shape as the magnetization direction is rotated. The effect was most pronounced in SD grains with tetrahedral morphology, where coercivities up to 120 mT were predicted. The equilibrium SD–SV threshold size in isolated particles with octahedral morphology was found by Witt et al. (2005) to be $d = 88$ nm, identical to that observed for cubic particles (d is defined here as the diameter of a sphere with the same volume as the particle). The similarity between the equilibrium SD–SV threshold size of cubes and that of octahedra is not surprising, since they have identical demagnetizing factors. There is a large difference, however, in the upper size limit for metastable SD states ($d = 320$ nm for octahedra versus $d = 160$ nm for cubes). This difference is illustrated further in Figure 36, in which the lower and upper limits

of stability for F states in cuboidal (Figure 36(a)) and non-cuboidal (Figure 36(b)) particles are compared. The particle morphologies that were used to produce Figure 36(b) are similar to those observed in many magnetotactic bacteria (Figure 36(c)) and are elongated along a $\langle 111 \rangle$ crystallographic direction. The shaded areas in Figure 36(a) and 36(b) show the range in the size and aspect ratio of magnetite crystals in natural magnetotactic bacteria that have this morphology (Petersen et al., 1989). A significant proportion of these particles lie above the upper limit of stability for F states predicted for cuboidal particles (Figure 36(a)). In cuboidal particles, magnetostatic interactions along the bacterial chain would be required to prevent the formation of vortex states. All of the particles, however, lie within the stability limit for F states for the more realistic particle morphologies (Figure 36(b)), implying that magnetostatic interactions may not be required to stabilize such states in large naturally occurring bacterial magnetosomes. The stabilization of F states in magnetosomes results in part from the elongation of the particles along $\langle 111 \rangle$ (so that magnetocrystalline and shape anisotropies act in unison) and in part from the more rounded ends of the crystals (which inhibit flowering and reduce the tendency to denucleate the F state). Nonuniform magnetization states have been observed in large magnetite magnetosomes using electron holography (McCartney et al., 2001).

2.24.4.2.2 Temperature dependence of domain states in isolated particles

The temperature dependence of magnetic domain states and the thermal relaxation properties of SD and PSD particles are of

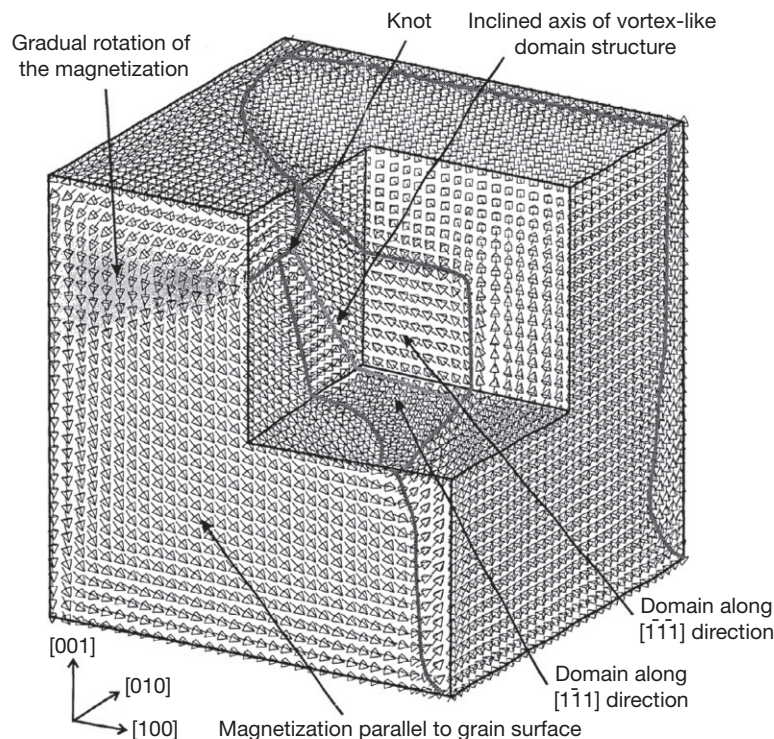


Figure 35 The magnetization structure of a $1\ \mu\text{m}$ cubic grain of magnetite with lines indicating the positions of major domain boundaries. The top surface shows a domain wall that is nucleated on a vortex core (labeled a knot in the diagram). The center of the grain is dominated by domains aligned toward an easy magnetocrystalline anisotropy axis, and the magnetization of the surface lies in the plane of the surface to reduce the magnetostatic free pole energy. Reproduced from Williams W and Wright TM (1998) High-resolution micromagnetic models of fine grains of magnetite. *Journal of Geophysical Research* 103: 30537–30550, with permission.

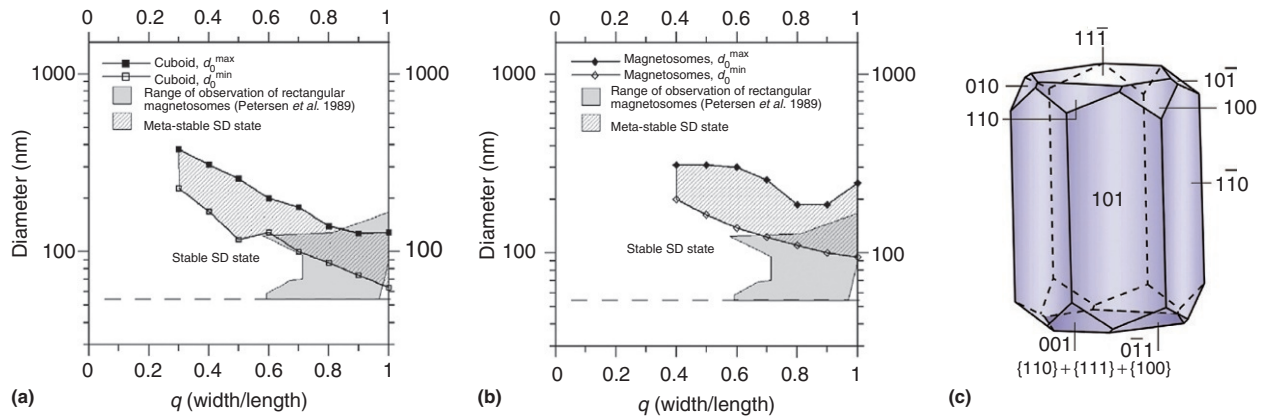


Figure 36 Calculated regions of stability and metastability of the SD state for magnetite. (a) Results for cuboidal particles. (b) Results for particles with morphologies similar to those seen in some strains of magnetotactic bacteria. (c) Displayed is the SD–PDS transition as a function of width over length of the respective particles. The shaded area delineates microscopically observed magnetosome shapes (Petersen et al., 1989). The dashed area corresponds to the calculated region where flower states are metastable. Above this area, the SD state is unstable and cannot persist. Parts (a) and (b) reproduced with permission from Witt et al. (2005). Part (c) modified from Bazylinski and Frankel (2004).

central importance to the theories of thermoremanent and viscous remanent magnetization (Néel, 1949). Most micromagnetic simulations are designed to minimize the internal energy of the system (eqn [43]) rather than its Gibbs' free energy. Consequently, the effective temperature of the simulations is 0 K, and the effects of entropy and thermal fluctuations are neglected. There are several ways of incorporating temperature into micromagnetic simulations. A basic approach, which neglects thermal fluctuations, is to use temperature-dependent values of A , K , and M_s in the calculation of the internal energy (Muxworthy and Williams, 1999; Muxworthy et al., 2003b). The temperature dependencies of A , K , and M_s in magnetite are given by Heider and Williams (1988), Fletcher and O'Reilly (1974), Abe et al. (1976), Bickford et al. (1957), Pauthenet and Bochirol (1951), Belov (1993), and Muxworthy and McClelland (2000). This approach allows the temperature dependence of equilibrium domain states to be determined but may incorrectly predict the existence of LEM states that would be unstable in the presence of thermal fluctuations. Thermal fluctuations can be incorporated into micromagnetic simulations by adding a random thermal field to the effective field (eqn [6]) and then determining the dynamic response of the system using the LLG equation (eqn [5]) (Fidler and Schrefl, 2000; Scholz et al., 2001). Alternatively, Monte Carlo methods can be used (Kirschner et al., 2005). Atomistic Monte Carlo simulations (see Section 2.24.2.2.1) are first used to determine the equilibrium spin configuration at a given temperature. The value of M_s to be used in the micromagnetic simulations is then obtained by averaging the spin configuration over the volume of one micromagnetic element. Thereafter, nonatomistic Monte Carlo techniques, analogous to those described in Section 2.24.2.2.1, are used to determine the equilibrium domain state of the micromagnetic model.

The lower and upper limits for the sizes of metastable F states in cubic magnetite particles at high temperatures are illustrated in Figure 37 (Muxworthy et al., 2003b). The equilibrium SD–SV threshold size increases from 70 nm at room temperature to approximately 90 nm close to the Néel temperature. The upper SD–SV threshold size increases from

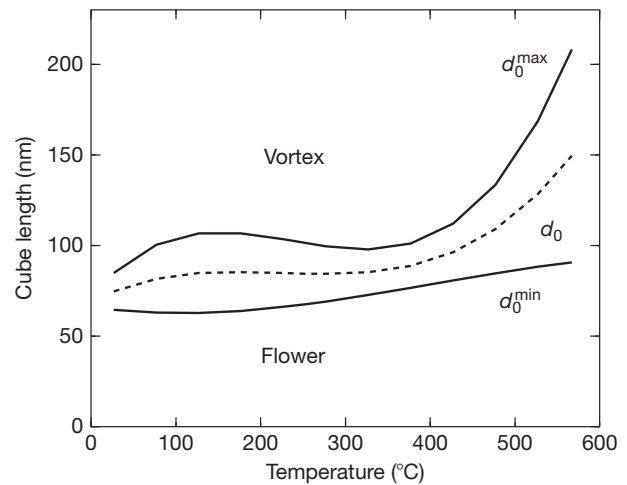


Figure 37 Calculated $d_0^{\max}$, d_0 , and $d_0^{\min}$ versus temperature for cubic grains of magnetite. Above $d_0^{\max}$, only the vortex state is possible, whereas below $d_0^{\min}$, only the flower or SD state is possible. Between $d_0^{\max}$ and $d_0^{\min}$, it is possible for the grain to be in either state. Reproduced from Muxworthy AR, Dunlop DJ, and Williams W (2003) High-temperature magnetic stability of small magnetite particles. *Journal of Geophysical Research* 108: 2281, with permission.

96 to ~200 nm close to the Néel temperature, considerably extending the size range over which metastable F states can exist. The SD–SV threshold size at low temperature (below the Verwey transition) has been explored by Muxworthy and Williams (1999). The large increase in the magnitude of the magnetocrystalline anisotropy at the Verwey transition (Abe et al., 1976; Muxworthy and McClelland, 2000) stabilizes the SD state with respect to the SV state, increasing the lower SD–SV threshold size to 140 nm at 110 K. However, the increase in magnetocrystalline anisotropy also increases considerably the height of the energy barrier that separates the SD and SV states, increasing the probability of particles becoming trapped in a metastable SV state on cooling below the Verwey transition. On the basis of experimental observations and

micromagnetic modeling, Kasama et al. (2012) and Bryson et al. (2012) demonstrated that ferroelastic twinning plays an important role in the stabilization of nonuniform magnetization states below the Verwey transition and suggested that such twinning is responsible for the field-memory effect, whereby the low-temperature hysteresis loop displays an inflection at a field equal to that that was applied during cooling (Smirnov, 2006a,b, 2007; Smirnov and Tarduno, 2002).

In order to calculate the thermal relaxation properties of SD and PSD particles, it is necessary to determine the magnitudes of the energy barriers that separate different LEM states. For SD particles, this can be done analytically (Newell, 2006a,b). For PSD states, energy barriers can be calculated using constrained micromagnetic simulations (Enkin and Williams, 1994; Muxworthy et al., 2003b; Winklhofer et al., 1997). In an unconstrained simulation, the magnetic moments of all of the elements are allowed to vary, so that the system evolves toward the nearest LEM state (Figure 34). In a constrained simulation, the system is forced to adopt a non-LEM state by fixing the orientations of the magnetic moments in some of the elements during the simulation (Figure 38). For example, by constraining the moments on opposite faces of a cuboidal

particle to be either parallel or antiparallel, it can be forced to adopt an F or an SV state, respectively (Figure 38(a)). Figure 38(b) and 38(c) shows the calculated energy of a particle with an aspect ratio 1:2 as the moments on opposite faces are rotated independently of each other through 360° (Muxworthy et al., 2003b). At 27°C (Figure 38(b)), the SV state is the AEM state, and there are two nondegenerate SD LEM states at 90° to each other. The SD state with the lower energy is magnetized parallel to the elongation direction of the particle. This state becomes the AEM state at 567°C (Figure 38(c)). The energy barriers that separate degenerate AEM states are illustrated in Figure 39 for two different particle sizes and aspect ratios (Muxworthy et al., 2003b). The relaxation time of such a particle is related to the height of the energy barrier, E_B (Winklhofer et al., 1997):

$$\tau = \tau_0 \exp\left(\frac{E_B(T)}{k_B T}\right) \quad [47]$$

where τ_0^{-1} ($\sim 10^9$ – 10^{10} Hz; McNab et al., 1968) is the frequency at which the particle attempts to switch its magnetization direction. The dashed lines in Figure 39 represent the blocking of remanent magnetization on laboratory

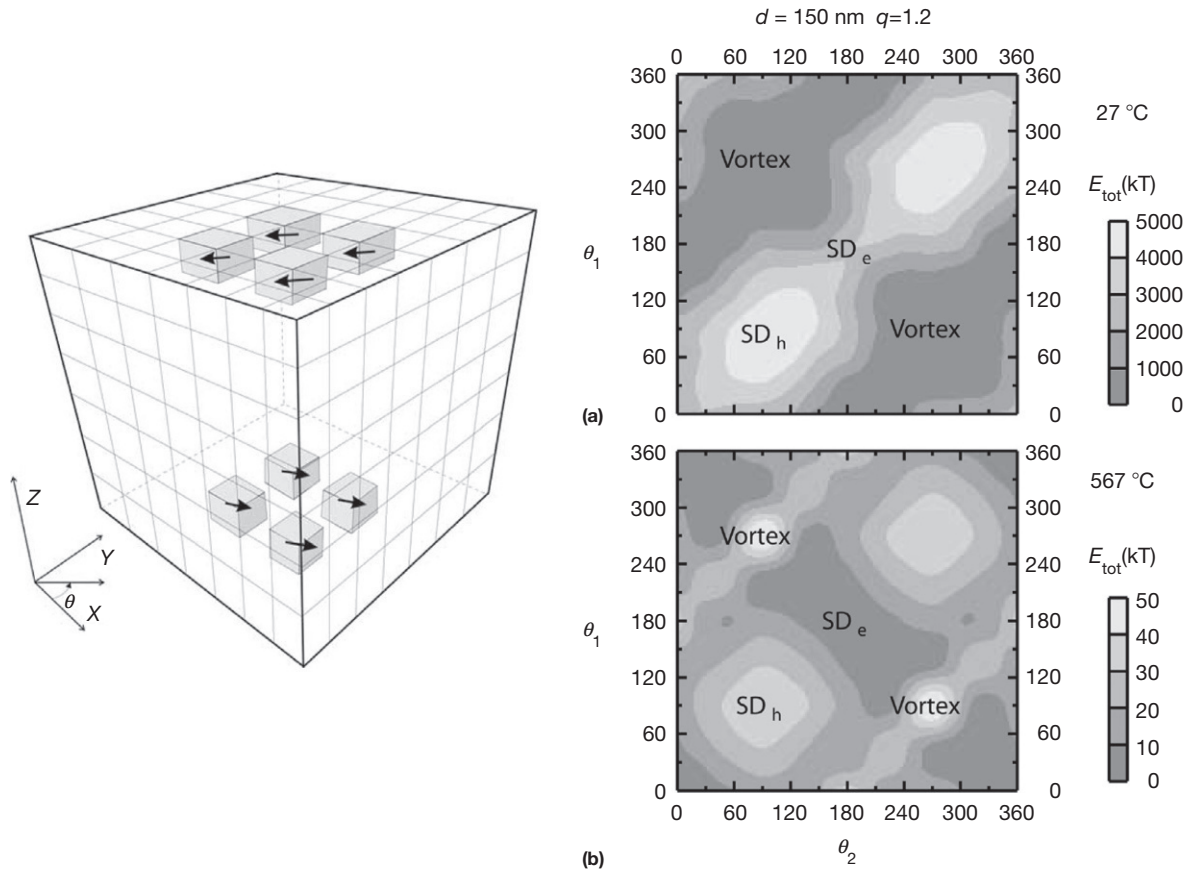


Figure 38 (a) Schematic of the constrained micromagnetic simulation. A number of cells at the top have their magnetization constrained to a direction θ_1 in the x - y -plane, while another set of cells at the bottom are constrained to a direction θ_2 also in the x - y -plane. θ_1 and θ_2 are set to angles between 0° and 360° at regular intervals. The energy is minimized with respect to the magnetization direction of all the other cells. Energy surfaces for a grain with edge 120 nm and aspect ratio 1:2 at (b) room temperature and (c) just below T_c . As the grain is asymmetric, there are hard (SD_h) and easy (SD_e) magnetic directions. Favorable vortex structures are also marked. Reproduced from Muxworthy AR, Dunlop DJ, and Williams W (2003) High-temperature magnetic stability of small magnetite particles. *Journal of Geophysical Research* 108: 2281, with permission.

($E_B \sim 25 k_B T$) and a geologic ($E_B \sim 60 k_B T$) timescales. The figure illustrates that blocking is more a function of the rapidly increasing energy barrier height on cooling, rather than of the decrease in thermal energy.

2.24.4.2.3 Field dependence of domain states

The effect of an external field can be included in micromagnetic simulations via eqn [35] and used to study hysteresis properties (Williams and Dunlop, 1995) and reversal mechanisms (Enkin and Williams, 1994) of individual PSD particles and the acquisition of saturation isothermal remanent magnetization and TRM (Muxworthy and Williams, 1999; Muxworthy et al., 2003b; Winklhofer et al., 1997) and to calculate the FORCs for both isolated grains and arrays of particles (Carvallo et al., 2003; Muxworthy and Williams, 2005; Muxworthy et al., 2004; see Section 2.24.5). Hysteresis loops are typically obtained by calculating a succession of quasistatic magnetic states, as the field is increased and decreased in a stepwise manner (Williams and Dunlop, 1995). This approach is valid so long as the damping of gyro-magnetic precession (eqn [5]) is much more rapid than the rate of increasing/decreasing field. PSD particles containing vortex states are observed to reverse their magnetization directions by a combination of gradual rotations of the outer moments and discontinuous reversals of the core moments (Williams and Dunlop, 1995).

2.24.4.2.4 Magnetostatic interactions between particles

Electron holographic observations of closely spaced particles (see Section 2.24.3.3.3) highlight the fundamental importance of magnetostatic interactions in determining the macroscopic properties of rocks and minerals. The complex problem of

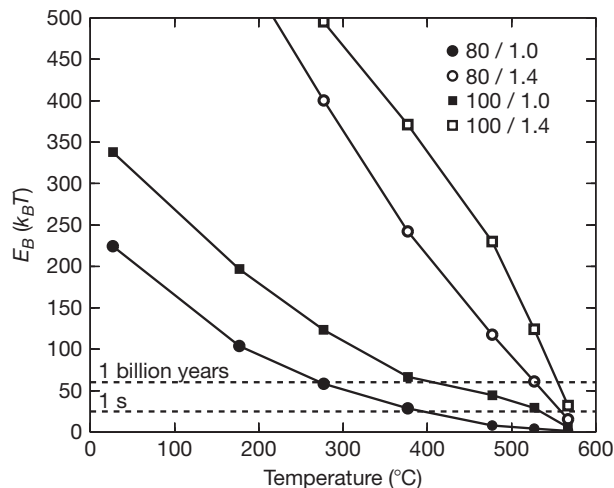


Figure 39 Calculated energy barrier (E_B) for magnetization reversal as a function of temperature for small particles of magnetite: two with $d = 80$ nm and aspect ratios of 1 and 1.4 (closed and open circles, respectively) and two for $d = 100$ nm and aspect ratios of 1 and 1.4 (closed and open squares, respectively). The two dashed lines at $E_B = 60 k_B T$ and $25 k_B T$ represent the paleomagnetic and laboratory stability criteria, respectively. Reproduced from Muxworthy AR, Dunlop DJ, and Williams W (2003) High-temperature magnetic stability of small magnetite particles. *Journal of Geophysical Research* 108: 2281, with permission.

determining the collective behavior of interacting arrays of magnetic particles has recently been tackled using micromagnetic simulations (Muxworthy et al., 2003a). Muxworthy et al. (2003a) performed a systematic study of saturation magnetization (M_s), saturation remanence (M_{rs}), coercivity (H_c), and coercivity of remanence (H_{cr}) as a function of particle size and spacing for regular 3-D arrays of cubic particles. The simulations were performed for different anisotropy schemes (uniaxial vs. cubic and aligned vs. random) to model a range of scenarios that are likely to be observed in natural systems. The results can be summarized on a 'Day plot' (Day et al., 1977; Dunlop, 2002a,b) of M_{rs}/M_s versus H_{cr}/H_c (Figure 40). For widely spaced particles (i.e., when the distance between particles is greater than five times their diameter), the effect of magnetostatic interactions is negligible, and the ratios of M_{rs}/M_s and H_{cr}/H_c converge to the ideal values for noninteracting particles ($M_{rs}/M_s = 0.5$ and 0.87 for randomly oriented uniaxial and cubic anisotropies, respectively; $H_{cr}/H_c = 1-1.5$). As the spacing between the particles is decreased, there is a consistent decrease in M_{rs}/M_s and increase in H_{cr}/H_c , which moves the system gradually from the SD to the PSD, and ultimately to the MD, regions of the Day plot (Figure 40). This prediction is consistent with the observation of interaction 'superstates' using electron holography (Figure 28), which are responsible for the PSD- and MD-like behavior of closely spaced SD particles in nanoscale intergrowths (Evans et al., 2006; Harrison et al., 2002). The effect

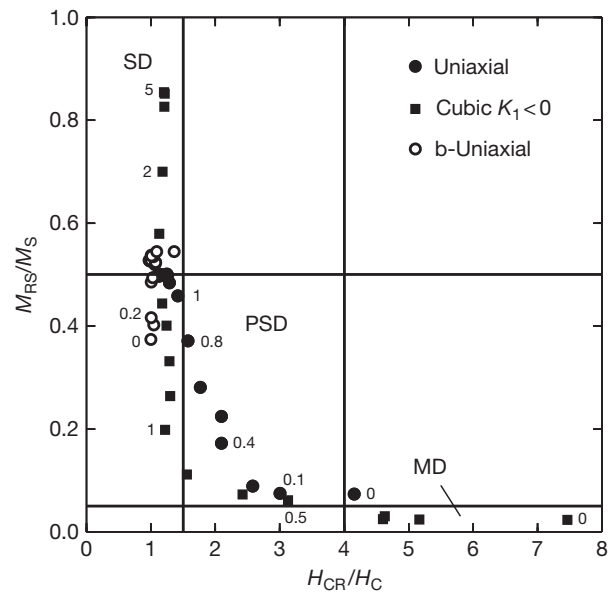


Figure 40 M_{rs}/M_s versus H_{cr}/H_c (Day plot) for three different anisotropy assemblages of ideal SD magnetite grains: uniaxial (closed circles), cubic $K_1 < 0$ (closed squares), and basal plane uniaxial (open circles), with a range of interaction spacing $0 \leq d \leq 5$, where d specifies the distance between adjacent particles in units of the particle width. For $d = 5$, particles are well separated and essentially noninteracting. For $d = 0$, the particles are just touching. Some of the interaction spacings are marked. The effect of interactions is fairly consistent, so unmarked intermediate points have intermediate value of d . The anisotropy orientation of the assemblage is random. Reproduced from Muxworthy AR, Dunlop DJ, and Williams W (2003) High-temperature magnetic stability of small magnetite particles. *Journal of Geophysical Research* 108: 2281, with permission.

of interactions on the properties of larger PSD particles is much more complex and can cause the system to adopt either more SD-like or more MD-like behavior, depending on the particle size, shape, and spacing and on the style of anisotropy. This behavior results in part from a shift of the SD–SV threshold with increasing interactions: particles that would adopt SV states in the absence of interactions are able to adopt SD states when they are interacting strongly with neighboring particles. Micromagnetic simulations suggest that this effect occurs when the easy axes of neighboring particles are well aligned, as is the case for chains of magnetite particles in magnetotactic bacteria (Figure 22) and for arrays of magnetic blocks formed by exsolution from an ulvöspinel host (Figure 26).

2.24.5 Magnetism at the Macroscopic Length Scale

In this final section, we review recent developments in the use of FORC diagrams to characterize the magnetic properties of rocks and minerals (Pike et al., 1999). Until recently, hysteresis loops

were the most widely used method of characterizing bulk magnetic properties (Roberts et al., 2000). However, parameters determined from hysteresis loops represent bulk averages and provide little information about the spectrum of coercivities and interaction fields that exist at the microscopic scale. The FORC diagram is a generalization of the well-known Preisach diagram (Preisach, 1935). The method requires the acquisition of many thousands of individual magnetization measurements and has only been made possible by the advent of fully automated vibrating-sample and alternating-gradient magnetometers (Flanders, 1988), which allow the rapid acquisition of magnetization data over a large range of temperatures and applied fields.

2.24.5.1 Theory

2.24.5.1.1 First-order reversal curves and the FORC distribution

The definition of a FORC is illustrated in Figure 41(a) (Pike et al., 1999; Roberts et al., 2000). Each FORC measurement begins by saturating the sample in a positive field. The external

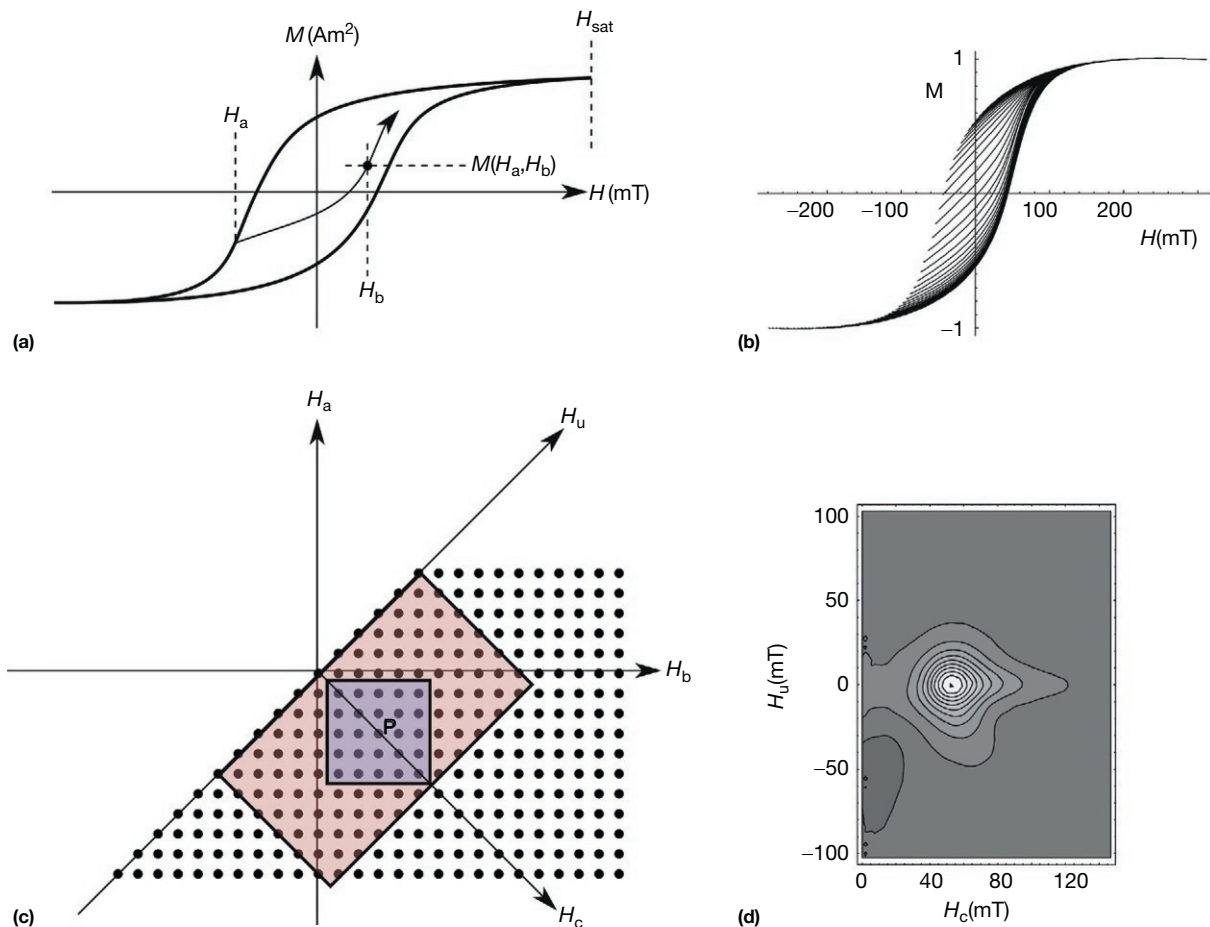


Figure 41 (a) Definition of a first-order reversal curve (FORC). (b) A set of FORCs for a sample of elongated SD maghemite particles at 20 K (reproduced with permission from Carvallo et al., 2004). (c) Matrix of H_a and H_b values used to measure magnetization during a typical FORC measurement. FORC diagrams are usually presented using a rotated set of axes H_u and H_c , covering the area of H_a – H_b space defined by the pink rectangle. The blue square represents the region of H_a – H_b space used to fit eqn [49] to $M(H_a, H_b)$ about a point P (SF = 2). (d) FORC diagram derived from the curves in (b). Reproduced from Carvallo C, Özdemir Ö, and Dunlop DJ (2004) First-order reversal curve (FORC) diagrams of elongated single-domain grains at high and low temperatures. *Journal of Geophysical Research* 109: B04105, with permission.

field is then decreased to some value, H_a (the reversal field), and the magnetization of the sample is measured as a function of increasing field, H_b , until positive saturation is reached again. A large number of FORCs are acquired for different reversal fields, in order to sample the entire area enclosed by a standard hysteresis loop (Figure 41(b)). Values of H_a and H_b are chosen to cover a regular grid in H_a – H_b space (Figure 41(c)), resulting in a magnetization matrix, $M(H_a, H_b)$. The FORC distribution is defined as the mixed second derivative of $M(H_a, H_b)$ with respect to H_a and H_b :

$$\rho(H_a, H_b) = -\frac{\partial^2 M(H_a, H_b)}{\partial H_a \partial H_b} \quad [48]$$

Note that in some studies, eqn [48] is multiplied by a factor of 1/2 (e.g., Newell, 2005; Pike, 2003). It is customary (see Section 2.24.5.1.2) to define a new set of axes, $H_c = (H_b - H_a)/2$ and $H_u = (H_a + H_b)/2$, as illustrated in Figure 41(c). The FORC diagram itself (Figure 41(d)) is a contour plot of $\rho(H_a, H_b)$, with H_c and H_u on the horizontal and vertical axes, respectively (covering the region of the H_a – H_b plane enclosed by the pink rectangle in Figure 41(c)).

In order to calculate the FORC distribution at any point P, a least squares fit to $M(H_a, H_b)$ is performed over a grid of points surrounding P (illustrated by the blue square in Figure 41(c)). The most common method used is that of Pike et al. (1999), in which the magnetization is fitted using a second-order polynomial function:

$$M(H_a, H_b) = a_1 + a_2 H_a + a_3 H_a^2 + a_4 H_b + a_5 H_b^2 + a_6 H_a H_b \quad [49]$$

The value of the FORC distribution at P is then equal to $-a_6$. The size of the grid is defined by a smoothing factor, SF, such that the grid extends over $(2SF + 1)^2$ points in the H_a – H_b plane. This method becomes inefficient as the total number of points in the $M(H_a, H_b)$ matrix increases. Heslop and Muxworthy (2005) described an alternative algorithm, based on the convolution method of Savitzky and Golay (1964), which yields identical results but is a factor of 500 times faster. Harrison and Feinberg (2008) adopted a method based on locally weighted regression smoothing, which allows automatic extrapolation across missing data. An increase in the SF leads to a smoothing of the FORC diagram. While some smoothing is necessary to reduce experimental noise, too much smoothing may unduly affect the form of the distribution. Heslop and Muxworthy (2005) described a numerical test, based on the examination of the autocorrelation function of the residual of observed and fitted values of $M(H_a, H_b)$, to determine the optimum value of SF. The optimum value depends on the resolution of the $M(H_a, H_b)$ matrix, but values in the range 2–5 are typically employed. The statistical significance of the FORC signal for a given smoothing factor can be calculated from an analysis of the fitting residuals (Heslop and Roberts, 2012). This information can guide measurement protocols and provides a more quantitative framework for the interpretation of FORC distributions. Because the $M(H_a, H_b)$ matrix does not extend to the $H_c < 0$ region (Figure 41(c)), increasing SF leads to an increase in the number of points close to the H_u axis that must be extrapolated (Carvallo et al., 2005). The need to extrapolate data can be overcome by the use of ‘extended’ FORCs (Pike, 2003), as described in Section 2.24.5.1.3.

2.24.5.1.2 Interpretation of the FORC diagram

FORC diagrams provide an alternative method of measuring the Preisach distribution, which yields information about the spectrum of coercivity and interaction fields within a sample (Carvallo et al., 2005; Mayergoyz, 1991; Preisach, 1935). The mathematical justification for using the Preisach model for interpreting FORC diagrams is described by Pike et al. (1999) and illustrated schematically in Figures 42 and 43. The system is assumed to consist of a collection of particles with either an irreversible (Figure 42(a)) or a reversible (Figure 42(b)) hysteresis loop (referred to as a ‘hysteron’). In the absence of an interaction field, irreversible particles switch their magnetization direction at the coercive field $\pm H_c$. In the presence of an interaction field, the hysteron is shifted to either the left or the right by an amount H_u , and switching now occurs at fields H_a and H_b (Figure 42(c)). H_a and H_b are related to the coercivity of the particle and the interaction field acting on it via $H_c = (H_b - H_a)/2$ and $H_u = (H_a + H_b)/2$. Each irreversible particle contributes to the FORC distribution at the corresponding point in H_c – H_u space (Figure 43). It is often assumed that the FORC distribution can be factorized into the product of two independent distributions:

$$\rho(H_c, H_u) = g(H_c)f(H_u) \quad [50]$$

where $g(H_c)$ describes the distribution of coercivities and $f(H_u)$ describes the distribution of interaction fields. Carvallo et al. (2004, 2005) measured FORC diagrams for a series of well-characterized SD and PSD particles and found eqn [50] to be valid. Muxworthy et al. (2004) and Muxworthy and Williams (2005) performed a similar test using FORC diagrams derived from micromagnetic simulations. Although they observed a

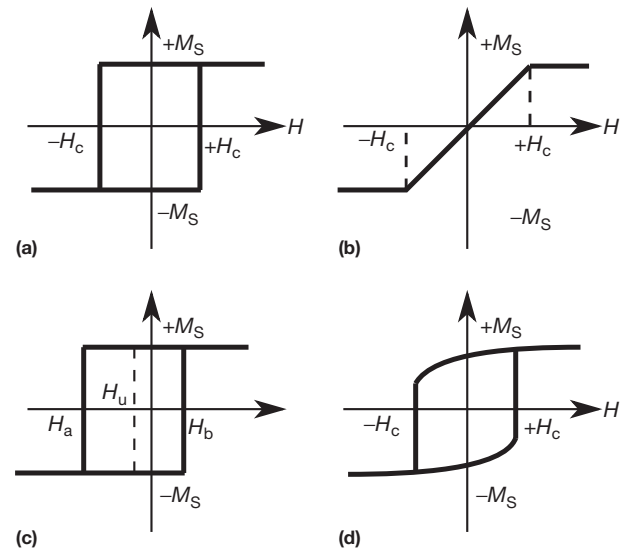


Figure 42 Magnetization as a function of applied field for particles with (a) irreversible and (b) reversible hysteresis loops. Irreversible switching occurs at an applied field of $\pm H_c$. (c) In the presence of a positive interaction field H_u , the irreversible hysteresis loop is shifted to the left, and switching now occurs at applied fields H_a and H_b . (d) A more general curvilinear hysteresis loop, which contains both reversible and irreversible magnetization components, can be used to explain the existence of negative peaks in SD FORC diagrams (Newell, 2005).

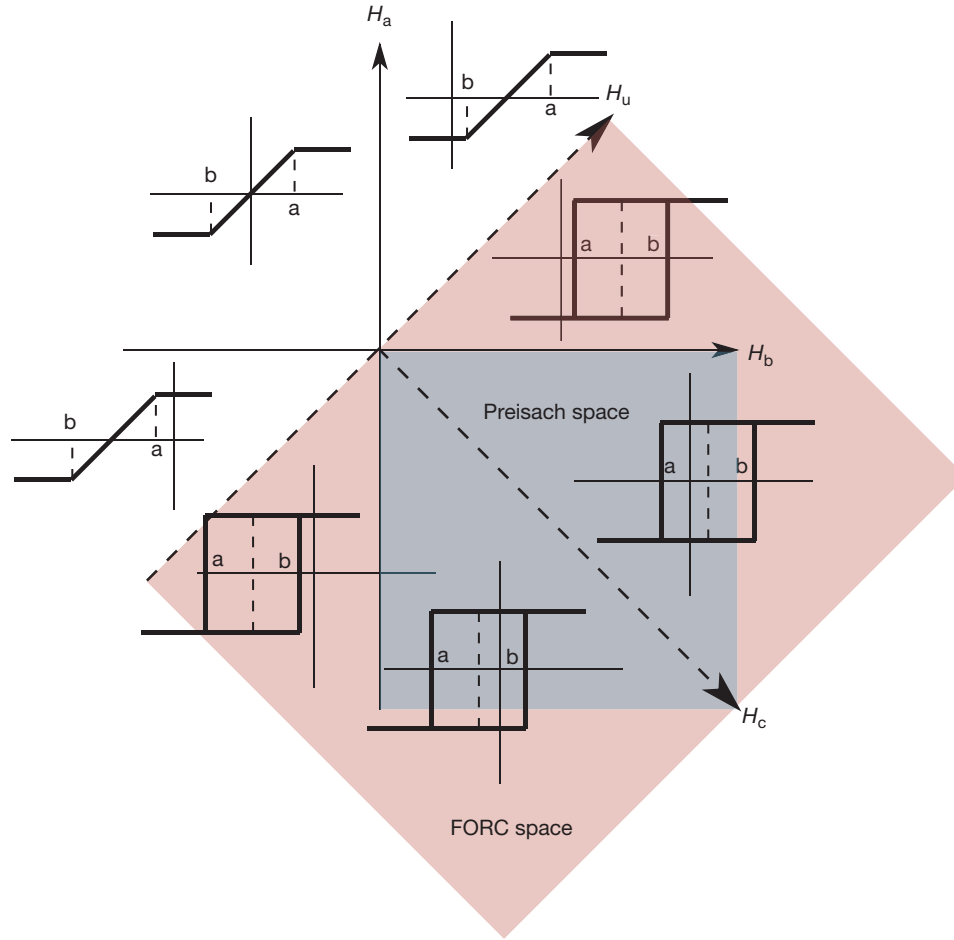


Figure 43 Form of the elementary reversible and irreversible magnetization cycles for different regions of the H_a – H_b plane. The gray area shows the region covered by a remanent Preisach diagram; the pink area is the region covered by a FORC diagram.

slight variation in H_c as a function of interaction strength, they concluded that eqn [50] provides a reasonable approximation for collections of SD particles with weak to moderate interactions. Analytic solutions for the effect of weak interactions on FORC diagrams are given by Egli (2006).

2.24.5.1.3 Extended FORCs and the reversible ridge

Reversible magnetization of the form shown in Figure 42(b) is normally absent from the FORC distribution, as its contribution disappears on taking the second derivative of $M(H_a, H_b)$. This problem can be overcome by the use of ‘extended FORCs’ (Pike, 2003; Pike et al., 2005). The magnetization matrix $M(H_a, H_b)$ is normally defined only in the region $H_b \geq H_a$ (as shown by the grid points in Figure 41(c)). However, $M(H_a, H_b)$ can be mathematically extended to cover the whole H_a – H_b plane:

$$H^*(H_a, H_b) = \begin{cases} M(H_a, H_b), & \text{if } H_b > H_a \\ M(H_a, H_a), & \text{if } H_b \leq H_a \end{cases} \quad [51]$$

By using M^* rather than M in eqn [48], the standard FORC diagram is obtained for $H_c > 0$, and a ‘reversible ridge’ is added

to the H_u axis, describing the distribution of reversible magnetization in the form

$$\rho(H_a, H_a) = \frac{1}{2} \delta(H_b - H_a) \left(\lim_{H_b \rightarrow H_a} \frac{\partial M(H_a, H_b)}{\partial H_b} \right) \quad [52]$$

Equation [52] describes the slope of the FORC with reversal field H_a , calculated at the point at which the FORC joins the major hysteresis loop (Pike et al., 2005). An example of an extended FORC diagram for a floppy disk recording material, including a profile of the reversible ridge, is shown in Figure 44. Since both the reversible and the irreversible components of magnetization contribute, the extended FORC distribution is properly normalized, such that the integral with respect to H_a and H_b equals the saturation magnetization of the sample (Pike, 2003). The finite resolution of real measurements, however, often shifts the reversible ridge into FORC space, where it overshadows low-coercivity FORC contributions (e.g., Figure 44(a)). This effect is particularly evident in samples where reversible magnetization processes are dominant. Alternative processing methods (e.g., Harrison and Feinberg, 2008) and extrapolation methods, such as the ‘slope extended’ FORC method (Egli et al., 2010), have been proposed to avoid the generation of a reversible ridge.

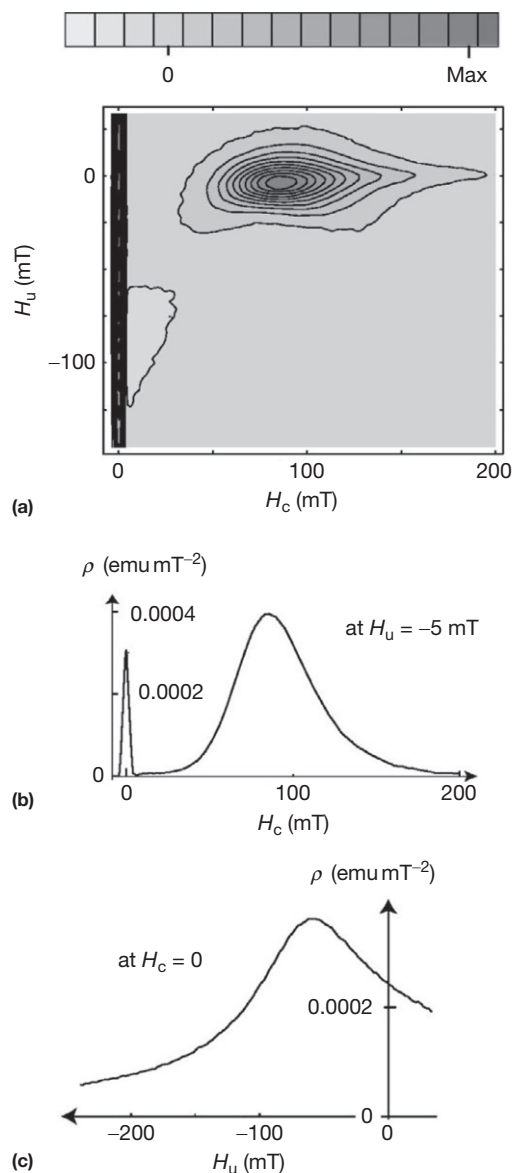


Figure 44 FORC diagram for a Sony floppy disk sample, showing the reversible ridge at $H_c = 0$. In the contour shading legend above the diagram, Max denotes the value of the FORC distribution at its 'irreversible' peak located at about $H_c = 90$ mT. A negative region occurs adjacent to the vertical ($H_c = 0$) axis at about $H_u = 85$ mT. Note that the high density of vertical contour lines near the $H_c = 0$ axis makes the shading there appear darker than it really is. (b) A horizontal cross section passing through the irreversible peak at $H_u = 5$ mT. The ridge at $H_c = 0$ can also be seen in this plot. (c) A vertical cross section through the reversible ridge at $H_c = 0$. Reproduced from Pike CR (2003) First-order reversal-curve diagrams and reversible magnetization. *Physical Review B* 68: 104424, with permission.

2.24.5.2 FORC Diagrams as a Function of Grain Size

2.24.5.2.1 SP particles

The expected form of the FORC diagram for SP particles is discussed by Pike et al. (2001a). Particles that are far above their blocking temperature have a reversible magnetization of the form shown in Figure 42(b) and do not contribute to a

normal FORC diagram (although they would contribute to the reversible ridge of an extended FORC diagram). Particles that are closer to their blocking temperatures show thermal relaxation of their magnetization state on a timescale similar to that of each FORC measurement step. This leads to contributions to the FORC distribution that peak around the origin and extend along the negative H_u axis (Figure 45). The form of the FORC diagram can be predicted using Néel theory of thermal relaxation in SD particles (Pike et al., 2001a).

2.24.5.2.2 SD particles

An analytic solution for the FORC diagram of ideal non-interacting particles with uniaxial anisotropy has been derived by Newell (2005) (Figure 46). For a collection of randomly oriented identical particles, the FORC function consists of two main contributions: a 'central ridge' signal that appears as a δ function along the H_c axis (Figure 46(a)) and a continuous signal that appears below the H_c axis only (Figure 46(b)). The central ridge is associated with the symmetrical irreversible switching of the particles, whereas the continuous part is associated with the reversible component of magnetization. The equivalent functions for the case of randomly oriented particles with a log-normal distribution of aspect ratios (i.e., a distribution of switching fields) are shown in Figure 46(c) and 46(d). The negative part of the continuous FORC function can be understood in terms of the 'curvilinear' form of the hysteron (Figure 42(d); Newell, 2005; Pike, 2003). In the Preisach model, the irreversible and reversible components of magnetization (Figure 42(a) and 42(b)) are completely independent. For a curvilinear hysteron, however, the reversible component of magnetic susceptibility decreases significantly as the particle switches from the upper to the lower branch of the loop. This coupling between the irreversible and reversible components gives rise to a systematic decrease, for a given $H_b < 0$, in the slopes of the FORCs as H_a decreases (Muxworthy et al., 2004). This, in turn, translates to a negative contribution to the FORC distribution.

A good source of uniaxial noninteracting SD particles is sediments containing fossil magnetotactic bacteria (Egli et al., 2010; Roberts et al., 2012). Figure 47 shows a high-resolution FORC diagram from a Lake Ely sediment sample (Egli et al., 2010) that displays all the predicted features of the Newell (2005) model, including a narrow central ridge with around one order of magnitude higher amplitude than the continuous signal. An analytic method for calculating the broadening of the central ridge caused by interparticle magnetostatic interactions is described by Egli (2006).

2.24.5.2.3 PSD particles

FORC diagrams for PSD size magnetite particles are described by Muxworthy and Dunlop (2002). FORC diagrams were measured for a series of synthetic magnetites with grain sizes varying from 0.3 to 11 μm (Figure 48). Small PSD particles have SD-like FORC diagrams, characterized by a closed positive peak at $H_c > 0$ and $H_u = 0$ (Figure 48(a)). With increasing grain size, the position of the peak shifts to lower H_c values (Figure 48(b)) and eventually moves to the origin (Figure 48(c)). This shift in peak position is accompanied by a spreading of the distribution in the H_u direction for small H_c (Figure 48(d)). Similar changes are seen as a function of temperature for particles of a fixed size. A diagnostic feature

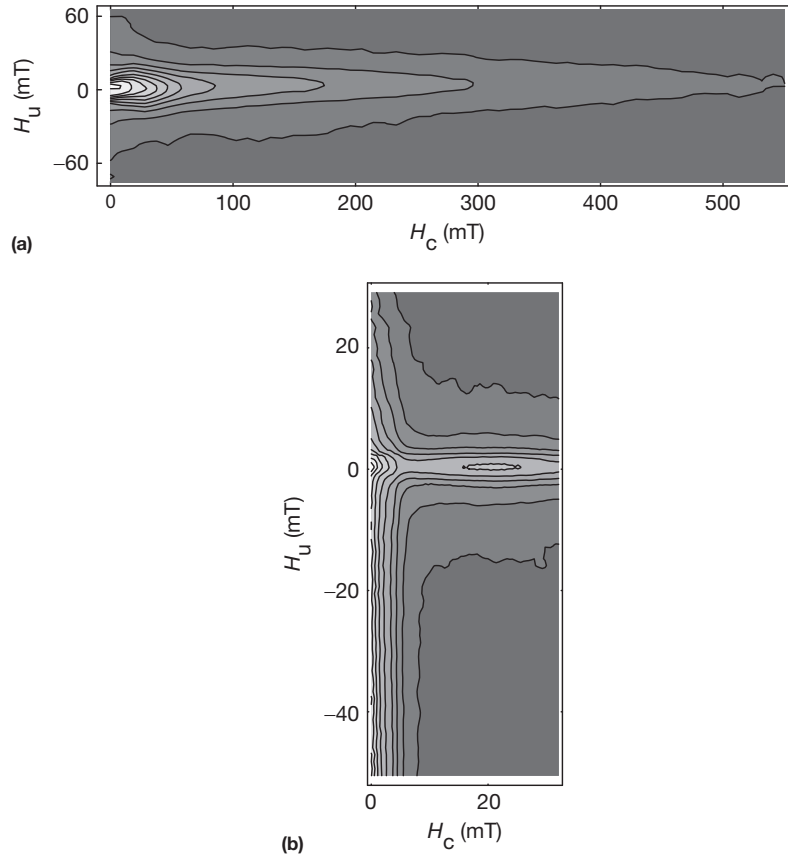


Figure 45 (a) FORC diagram for an SP hematite-bearing Aptian red-bed sample from the south of France. (b) High-resolution FORC diagram for the lower left-hand portion of the FORC plane for the same sample. Reproduced from Pike CR, Roberts AP, and Verosub KL (2001) First-order reversal curve diagrams and thermal relaxation effects in magnetic particles. *Geophysical Journal International* 145: 721–730, with permission.

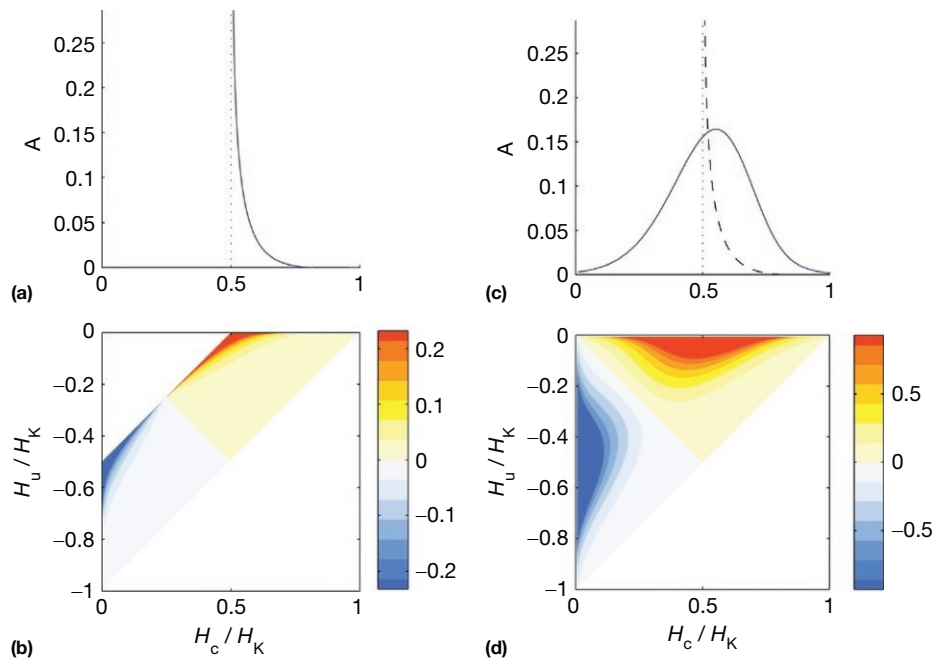


Figure 46 (a) Magnitude of the central ridge FORC signal observed along the H_c axis for a randomly oriented assemblage of identical uniaxial particles with axial ratio 2, plotted versus H_c/H_K , where H_K is the anisotropy field. Note the minimum switching field is $0.5 H_K$, as predicted by the Stoner–Wohlfarth model. (b) The continuous part of the FORC function for the same particles as (a). Note both positive and negative regions separated by the line $H_u = -H_c$. (c) and (d) equivalent plots to (a) and (b) but for a log-normal distribution of axial ratios (average value 2 and standard deviation 0.25). Reproduced after Newell A (2005) A high-precision model of first-order reversal curve (FORC) functions for single-domain ferromagnets with uniaxial anisotropy. *Geochemistry Geophysics Geosystems* 6: Q05010, with permission.

of the FORC diagram for samples dominated by SV states is the so-called 'butterfly' structure identified by Pike and Fernandez (1999) and Dumas et al. (2007) (Figure 49). This feature is associated with the nucleation and annihilation fields for

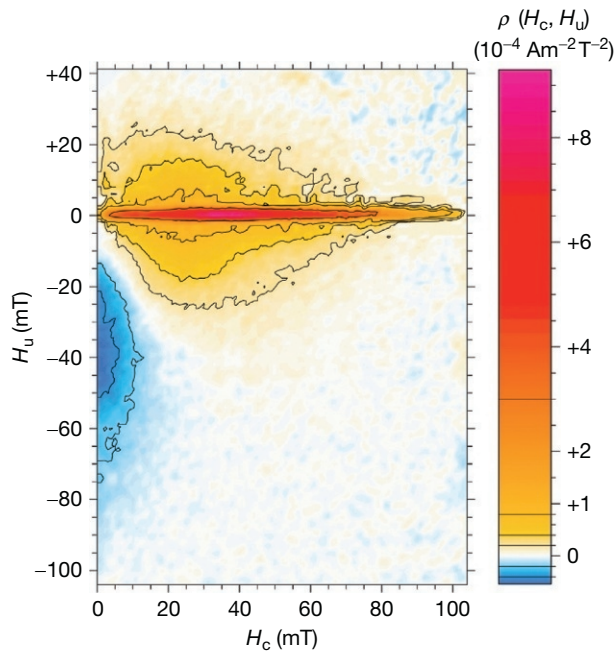


Figure 47 High-resolution FORC diagram for a sediment sample from Lake Ely (Pennsylvania) containing magnetotactic bacteria. Note the one order of magnitude difference between the amplitude of the central ridge and the remaining part of the diagram. The color scale is chosen so that zero is white, negative values are blue, and positive values are yellow to red. Contour lines are drawn for values specified in the color scale bar. Measurements are not normalized by mass. Reproduced from Egli R, Chen AP, Winklhofer M, Kodama KP, and Horng C (2010) Detection of noninteracting single domain particles using first-order reversal curve diagrams. *Geochemistry Geophysics Geosystems* 11: Q01Z11, <http://dx.doi.org/10.1029/2009GC002916>, with permission.

vortices nucleating on opposite sides of a particle. Lappe et al. (2011) identified the butterfly structure in the FORC diagrams of metallic Fe nanoparticles that had been shown to contain SV states via electron holography. Based on the theory of Pike and Fernandez (1999), they were then able to determine the range of nucleation and annihilation fields for the samples ($H_N = 58 \pm 55$ mT and $H_A = 170 \pm 55$ mT). Such information is important in determining the paleomagnetic properties of Fe nanoparticles in meteorites.

2.24.5.2.4 MD particles

Theoretical predictions and experimental measurements of the FORC diagrams for noninteracting MD particles are described by Pike et al. (2001b) and Church et al. (2011). 1-D models of domain wall pinning predict FORC diagrams consisting of perfectly vertical contours, with the value of the FORC distribution decreasing smoothly with increasing H_c . This model agrees well with experimental measurements on annealed (i.e., stress-free) magnetite samples (Figure 50). The vertical spread of the FORC function results from the fact that each particle contains a large number of pinning sites at which a domain can be trapped during the FORC measurement. These different pinning sites can be represented by an equivalent number of hysterons, which are spread out along the H_u axis by the self-demagnetizing field (Pike et al., 2001b). FORC diagrams for unannealed MD samples are similar to those observed at the upper end of the PSD range (compare, e.g., Figure 50(c) with Figure 48(d)).

2.24.5.3 Mean-Field Interactions and FORC Diagrams

In the most basic form of the Preisach model, the distribution of interaction fields is assumed to be static. In reality, however, the field acting on each particle is the sum of the stray fields created by all the other particles in the system and will vary as the overall magnetization of the system changes (Egli, 2006). In general, both the mean value and the standard deviation of the interaction field distribution (IFD) are functions of the net

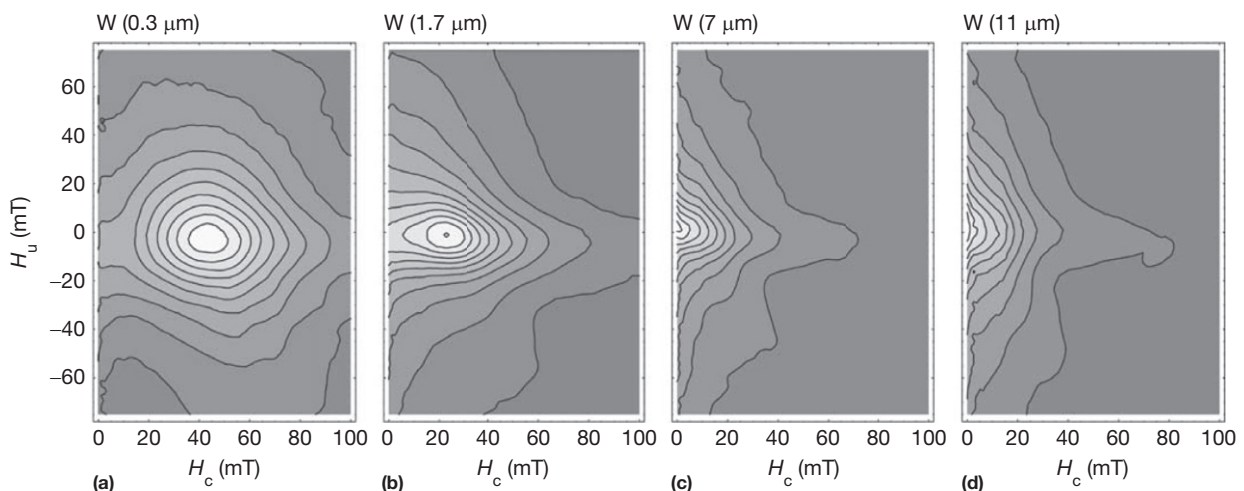


Figure 48 FORC diagrams for a series of synthetic PSD magnetite samples with grain sizes of (a) 0.3 μm , (b) 1.7 μm , (c) 7 μm , and (d) 11 μm . Reproduced from Muxworthy AR and Dunlop DJ (2002) First-order reversal curve (FORC) diagrams for pseudo-single-domain magnetites at high temperature. *Earth and Planetary Science Letters* 203: 369–382, with permission.

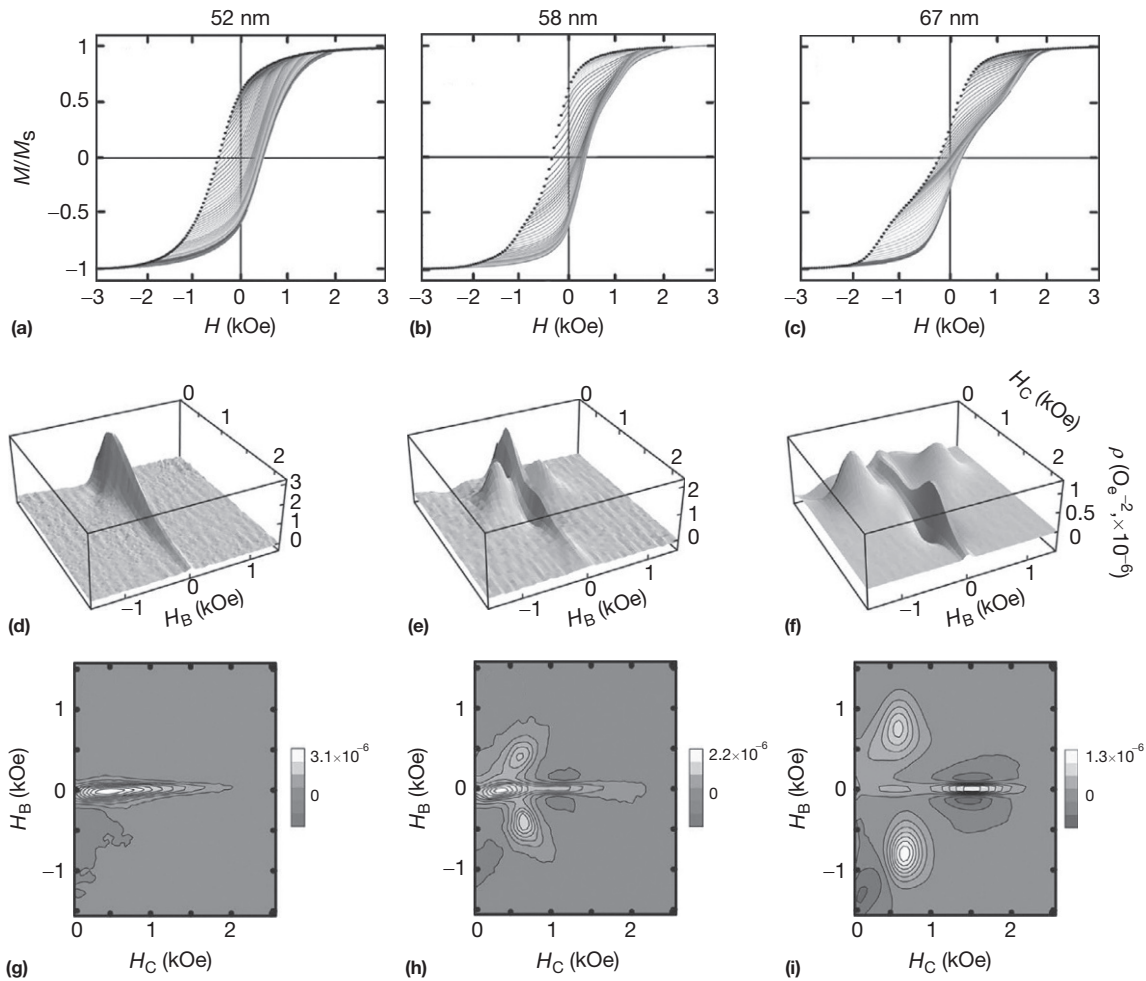


Figure 49 FORCs and the corresponding distributions for collections of metallic Fe nanodots with different diameters spanning the SD–SV transition. Families of FORCs, whose starting points are represented by black dots, are shown in (a–c) for 52, 58, and 67 nm diameter Fe nanodots, respectively. The corresponding FORC distributions are shown in 3-D plots (d–f) and contour plots (g–i). The characteristic features seen in (h) and (i) are caused by transitions between SD and SV states in the larger nanodots. The butterfly-shaped feature, consisting of a positive peak on the H_c axis flanked above and below by negative peaks, is caused by differences in the nucleation and annihilation field for vortices appearing on either side of the particles (Pike and Fernandez, 1999). Reproduced after Dumas RK, Li C, Roshchin IV, Schuller IK, and Liu K (2007) Magnetic fingerprints of sub-100 nm Fe dots. *Physical Review B* 75: 134405, with permission.

magnetization of the system (the ‘variable-variance moving Preisach’ model). For example, if a collection of particles is fully saturated in a large magnetic field, each particle experiences roughly the same mean-field interaction and the standard deviation of the IFD tends to zero. In the demagnetized state, each particle will experience a different interaction field; the mean value of the IFD is now zero and the standard deviation is maximum. The constant of proportionality relating the mean-field interaction to the net magnetization of the system is referred to as the ‘moving parameter,’ α , which can be either positive or negative, depending on the geometry of the system (Stancu et al., 2001, 2003). Positive α implies that the mean field has a magnetizing effect and leads to a spontaneous mutual alignment of the particles. This case applies, for example, to the chains of magnetite particles in magnetotactic bacteria (Figure 22). Negative α implies that the mean field has a demagnetizing effect. This case applies, for example, to perpendicular recording media (i.e., planar arrays of SD

particles that have their easy axes perpendicular to the plane). The FORC diagram for such a system, composed of a perpendicular array of Ni pillars, is shown in Figure 51 (Pike et al., 2005). The ‘wishbone’ form of the FORC diagram has two main peaks: one occurring at low H_c and $H_u > 0$ and one occurring at high H_c and $H_u = 0$. The distance between these two peaks in the H_c direction yields information about the range of coercivities in the system. The displacement of the first peak in the positive H_u direction yields information about the strength of the mean-field demagnetizing interaction.

2.24.5.4 Practical Applications of FORC Diagrams

The FORC method has been applied in rock magnetism as a method of characterizing the magnetic mineralogy of natural samples (Roberts et al., 2000), identifying mixtures of soft and hard magnetic minerals (Muxworthy et al., 2005), and identifying magnetostatic interactions as a preselection tool for

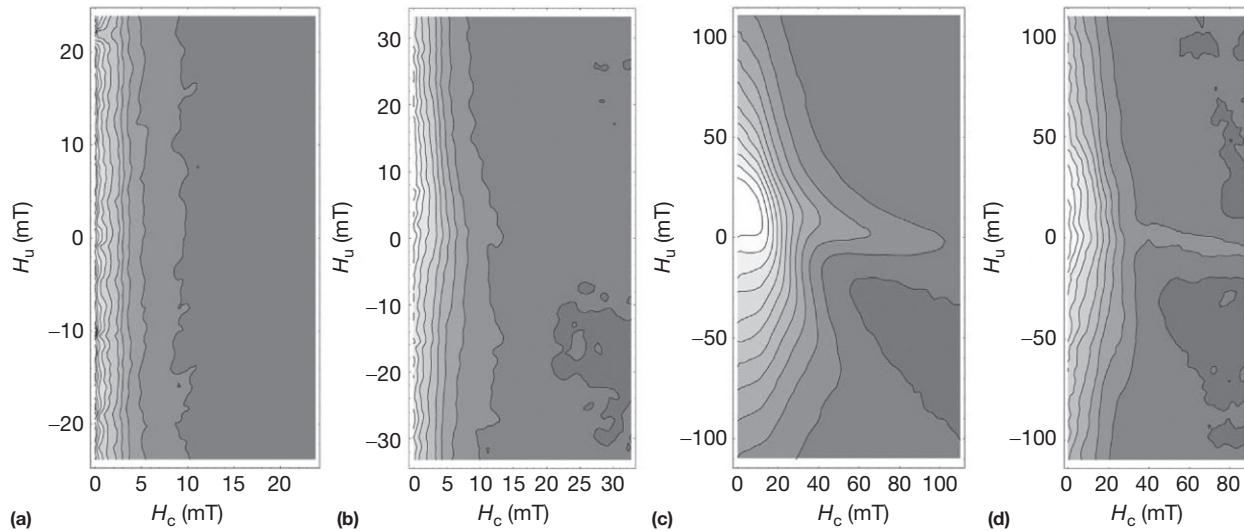


Figure 50 FORC diagrams for a series of MD samples. (a) A sample of M80 transformer steel. (b) A 2 mm grain of magnetite, after annealing. (c) The same 2 mm grain of magnetite before annealing. (d) An unannealed 125 μm magnetite grain. Reproduced from Pike CR, Roberts AP, Dekkers MJ, and Verosub KL (2001) An investigation of multidomain hysteresis mechanisms using FORC diagrams. *Physics of the Earth and Planetary Interiors* 126: 11–25, with permission.

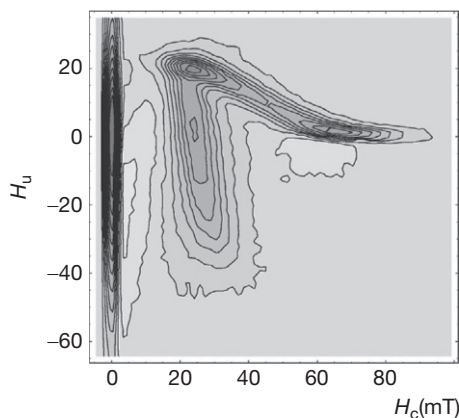


Figure 51 FORC diagram for a perpendicular recording medium, composed of a perpendicular array of Ni pillars. Reproduced from Pike CR, Ross CA, Scalettar RT, and Zimanyi G (2005) First-order reversal curve diagram analysis of a perpendicular nickel nanopillar array. *Physical Review B* 71: 134407, with permission.

paleointensity studies (Wehland et al., 2005). Pan et al. (2005) had used FORC diagrams to determine the strength of magnetostatic interactions in concentrated samples of magnetotactic bacteria (Figure 52). The FORC distribution has large SD-like peak centered on $H_c \sim 40$ mT and displaced slightly in negative H_u direction. The vertical spread of the IFD has a FWHM of just 6.3 mT, much lower than the ideal intrachain interaction field of 60 mT. This observation demonstrates that the magnetosome chains are effectively behaving as elongated SD particles and switch as a single unit. In such cases, the interaction fields measured by the FORC method provide an indication of inter-chain and intercellular interactions. The small peak in the FORC distribution about the origin can be attributed to the smaller magnetosomes that commonly occur at the ends of the chain. The observation of a narrow central ridge (i.e., one with a width

that is limited by the resolution of the measurement itself) is diagnostic of noninteracting particles, which in turn is often associated with intact magnetosome chains. FORC diagrams are becoming an increasingly powerful method of identifying fossil magnetotactic bacteria in sediments and demonstrate that magnetofossils are much more prevalent in nature than previously thought (Roberts et al., 2012). FORC diagrams are increasingly being used to derive quantitative information about the fundamental magnetic mineralogy of a sample – information that can be used as empirical input into physical simulations of the paleomagnetic remanence acquisition process (Muxworthy and Heslop, 2011; Muxworthy et al., 2011). If the sample carries a TRM, a comparison of observed versus simulated remanence can be used to estimate the intensity of the magnetizing field, without the need to heat the sample (as is the case for traditional paleointensity measurements). Such nonheating paleointensity methods are principally of interest in the analysis of extraterrestrial materials, where heating of the sample either is not permitted on curatorial grounds or would lead to excessive thermal alteration of the sample. Although in their infancy, such methods have the potential to improve our understanding of the principles and limitations of current paleomagnetic theories and, in combination with the other techniques outlined in this chapter, to extend these beyond the limits of SD theory.

2.24.6 Summary

Now is a very exciting time for the field of rock and mineral magnetism. The discovery of large-amplitude magnetic anomalies on Mars (Acuna et al., 1999; Connerney et al., 1999, 2004) has ignited a general interest in the effect of nanoscale microstructures on the origin and stability of planetary-scale magnetic anomalies. Conventional wisdom that these anomalies are due to the induced magnetization of MD magnetite is now being challenged in light of the Mars magnetic survey. Mars no longer generates its own magnetic field; the anomalies are purely

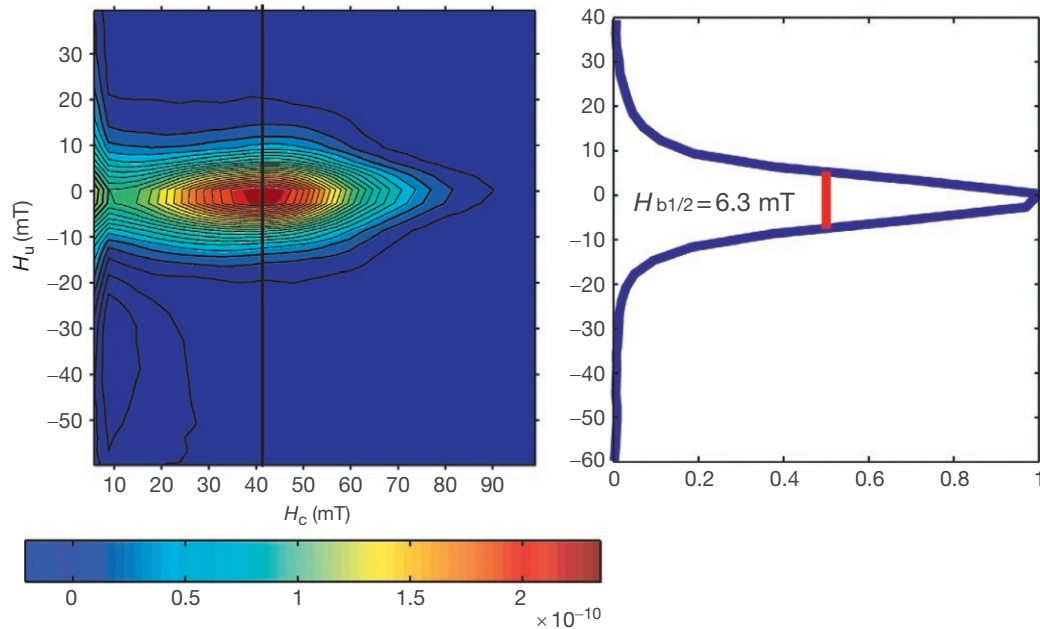


Figure 52 FORC diagram of a concentrated sample of magnetotactic bacteria. The FORC distribution of the MTB sample is bimodal with a broad maximum centered at 42 mT and a sharper peak toward the $H_c = 0$ axis. The latter is attributed to emerging magnetosomes at the chain ends. (b) Vertical profile through the high-coercivity peak of the distribution with mean half width field of 6.3 mT at $H_c = 41.4$ mT. Reproduced with permission from Pan Y, Petersen N, Winklhofer M, et al. (2005) Rock magnetic properties of uncultured magnetotactic bacteria. *Earth and Planetary Science Letters* 237: 311–325.

remanent in origin – faithfully recorded by magnetic minerals over 4 billion years ago (at a time when Mars did generate a field) and maintained without significant decay until the present day. The minerals responsible for the anomalies on Mars – and how they maintain such strong remanence over time – are currently the subject of intense speculation.

The techniques described in this chapter allow such problems to be tackled from both experimental and theoretical viewpoints, encompassing the entire range of length scales of interest, from atomistic interactions to planetary-scale magnetic anomalies. Since the dominant carriers of stable NRM are SD particles with sizes in the range 30–200 nm, techniques such as electron holography (Section 2.24.3) have the potential to revolutionize the way rock magnetic measurements are made in the future. By using the 3-D morphologies of magnetic nanoparticles, provided by electron tomography, as the input for finite element micromagnetic simulations (Section 2.24.4), it is now possible to compare experimental observations and theoretical predictions directly. Differences between observed and calculated behaviors are likely to be the result of atomistic effects at surfaces, interfaces, and defects. Ultimately, the application of atomistic simulations (Section 2.24.2) will permit the influence of such atomic-scale features on standard rock magnetic analysis (Section 2.24.5) to be determined.

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2.25 Properties of Rocks and Minerals – The Electrical Conductivity of Rocks, Minerals, and the Earth

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Glossary

Activation energy Energy barrier for a thermally activated process.

Archie's law Relationship between bulk electrical conductivity and fluid or melt conductivity of a porous fluid- or melt-containing composite medium, of the form $\sigma_{\text{bulk}} = \sigma_{\text{melt}} C X_m^a$, where X_m is volume fraction fluid or melt and C and a are constants.

Bulk conductivity Average electrical conductivity of a composite medium.

D+ model A conductivity–depth model consisting of a sequence of delta functions in an insulating half-space.

Conductance Product of electrical conductivity and thickness. SI units of Siemens (S).

Electrical conductivity A physical constant σ relating electrical current density to the electrical field strength. The SI unit of conductivity is Siemens per meter (S m^{-1}) where $1 \text{ S} = 1 \Omega^{-1}$, so it is also expressed as $\Omega^{-1} \text{ m}^{-1}$.

Electrical resistivity Reciprocal of electrical conductivity. SI units of (Ωm).

Electromagnetic skin depth The depth at which electromagnetic fields are attenuated to $1/e$ of their surface values. Depends on electrical conductivity of the medium and the frequency of the electromagnetic waves.

Impedance phase Phase difference between the electric and magnetic fields.

Magnetotellurics Method of determining the electrical conductivity structure of the Earth by measuring time variations of the electrical and magnetic field at the surface.

Point defects Imperfections in a crystal lattice where an atom or ion is missing or is in an irregular site.

Polaron Point defect in a crystal in which a Fe^{3+} ion substitutes on a Mg^{2+} site.

Vacancy Crystal lattice location where an atom or ion should be but is missing.

Nomenclature

D Diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)

H_y Horizontal component of magnetic field (T)

E_a Activation energy (kJ mol^{-1})

E_x Horizontal component of electrical field (V m^{-1})

$\text{Fe}_{\text{Mg}}^\bullet$ Small polaron, Fe^{3+} on an Mg^{2+} site

f_{O_2} Oxygen fugacity (Pa)

h Electron hole

k Boltzmann's constant, $1.3807 \times 10^{-23} \text{ J K}^{-1}$

q Electrical charge (C)

$V_{\text{Mg}}^\bullet$ Magnesium vacancy

ΔV_σ Activation volume for electrical conduction ($\text{m}^3 \text{mol}^{-1}$)

σ Electrical conductivity (S m^{-1})

ρ Electrical resistivity (Ωm)

τ Period (of a sinusoidal wave) (s)

μ Electrical mobility ($\text{m}^2 \text{V}^{-1} \text{s}^{-1}$)

2.25.1 Introduction

The study of the electrical properties of minerals and rocks is of broad interest in the Earth and planetary sciences. Magnetotelluric (MT) and geomagnetic depth sounding (GDS) studies yield electrical conductivity versus depth models for the Earth. Laboratory measurements of the electrical conductivity of candidate minerals under relevant conditions with accompanying theoretical understanding are needed to interpret the field results. In principle, electrical conductivity results are complementary to seismic results because conductivities of materials are highly sensitive to defects, minor impurities (including hydrogen in minerals), anisotropy, presence of highly conducting melts or fluids, and the distribution or texture of those melts or fluids, features that might not yield strong seismic anomalies. In this report, we focus on the electrical conductivity of mantle materials, including recent work incorporating hydrogen, and related field studies. It is not always possible to tease out unambiguous interpretations from field results in terms of the all the possible mineral physics parameters. As laboratory and field studies advance, it is possible to narrow the range of interpretations. Electrical conductivity studies are attractive as a potential sensor of hydrogen in the mantle.

2.25.2 Electrical Conductivity of Materials

2.25.2.1 Point Defects and Conductivity

The electrical conductivity of minerals is governed by the point defect chemistry. Point defects are imperfections in the crystal lattice, such as substitutions, vacancies, interstitial ions, electrons, and electron holes (electron deficiencies in the valence band commonly termed 'holes'). Kroger-Vink notation describes the type of defect and its effective charge relative to a normal lattice site. Each defect is indicated by the symbol A_B^c , in which the main symbol A indicates the species of the defect (element/ion, electron e , hole h , or vacancy V), the subscript B indicates the type of site (normal lattice site of a particular ion or an interstitial site I), and the superscript c indicates the net effective charge of the defect relative to the normal occupancy of that lattice (where dots indicate positive relative charge, slashes indicate negative relative charge, and 'x' indicates zero relative charge). Thus, for a magnesium-iron silicate mineral, V_{Si}^{4-} is a silicon vacancy (with a charge of -4 relative to a site occupied by a silicon ion), Fe_{Mg}^x is a magnesium site containing an Fe^{2+} ion (neutral with respect to the normal site occupancy), $Fe_{Mg}^{\bullet}$ is a magnesium site containing an Fe^{3+} ion (relative charge of $+1$ relative to a site occupied by Mg^{2+}), V_{Mg}^{2-} is a magnesium vacancy (relative charge of -2 relative to a site occupied by Mg^{2+}), and O_O^x is an oxygen site containing an O^{2-} ion.

The electrical conductivity of a material can be represented as the sum of the conductivity contributions of each charge carrier (or defect) type acting independently (in parallel):

$$\sigma = \sum \sigma_i = \sum c_i q_i \mu_i \quad [1]$$

where c_i is the concentration of the i th type of charge carrier, q_i is its effective charge (coulomb), and μ_i is its mobility (typically

in $m^2 V^{-1} s^{-1}$). Defects are present in all crystal structures and each contributes to the total conductivity. Perturbation of the concentration of one defect can influence the concentrations of the others, so the concentrations may not be completely independent. Usually, only one or two types of defects dominate under a given set of thermodynamic conditions. Chemical reactions between defects can be written to express their concentrations in terms of equilibrium constants. For example, removing a positively charged ion from its normal site results in the formation of a vacancy plus an interstitial ion (formation of a Frenkel defect) and can be written as



For such a reaction, the chemical equilibrium constant K is written as

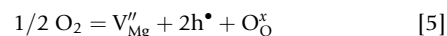
$$K = \frac{[V_A'] [A_I]}{[A_A^x]} \quad [3]$$

where the square brackets indicate site fractions. The Gibbs free energy ΔG_0 for this reaction is given by

$$\Delta G_0 = -RT \ln K \quad [4]$$

in which R is the gas constant and T is absolute temperature.

Reactions incorporating oxygen from the surroundings are important in oxide materials. For example, in MgO , the reaction



describes the incorporation of oxygen to form a magnesium vacancy, a hole h , and an oxygen on a normal lattice site. The equilibrium constant for this reaction is

$$K = \left[V_{Mg}^{2-} \right] [h]^2 [O_O^x] / f_{O_2}^{1/2} \quad [6]$$

Thus, the magnesium vacancy concentration in pure MgO depends on f_{O_2} (at constant temperature). Even in the presence of relatively small amounts of impurity ions, the concentrations of defects (and hence the conductivity) may vary greatly. This extreme sensitivity of defect concentration to minor and trace element concentrations makes it very difficult to establish absolute values for the conductivities of 'pure' minerals, especially at low temperatures. In the laboratory, one tries to determine which defect or defects dominate conduction under a given set of conditions by determining conductivity under varying conditions of temperature, oxygen fugacity, trace element concentration, and/or other variables. In addition, determination of the Seebeck coefficient (thermoelectric coefficient) can identify the charge of dominant conducting species. The results are then combined with defect reactions such as [3] and [5] above and defect conservation laws such as conservation of mass, charge neutrality, and lattice sites to determine the particular defect reaction that controls the concentration of the dominant defect and predicts the dependence on other environmental conditions (f_{O_2} in particular). Materials science reference works such as Kröger (1974) and Kingery et al. (1976) describe this process for many materials and references such as Stocker (1978), Stocker and Smyth (1978), and Hirsch and Shankland (1993) describe defect equilibria in some important Earth materials (see also Tyburczy and Fislis, 1995).

To completely specify the thermodynamic state of a defect-containing crystal, the Gibbs phase rule must be satisfied. For a three-component system, such as (Mg,Fe)O, this constraint means that the temperature, the pressure, the oxygen fugacity, and the Mg/Fe ratio in the solid must all be specified. Thus, the conductivity will have the general form

$$\sigma_i = \sigma_o \exp(-E_a/kT) \left(\text{Fe}_{\text{Mg}}^x \right)^m f_{\text{O}_2}^n \quad [7]$$

in which Fe_{Mg}^x is the fraction of Fe on Mg sites and n and m are constants from the defect reaction stoichiometry. For a four-component system, such as olivine $(\text{Mg,Fe})_2\text{SiO}_4$, an additional constraint must be specified; the most frequently specified constraint is the silica activity a_{SiO_2} (or equivalently the enstatite activity a_{En}),

$$\sigma_i = \sigma_o \exp(-E_a/kT) \left(\text{Fe}_{\text{Mg}}^x \right)^m f_{\text{O}_2}^n a_{\text{SiO}_2}^p \dots \quad [8]$$

in which p is also a constant. One goal of experimental studies is to determine the exponents m , n , and p for the dependence of conductivity on compositional and environmental parameters, but all the parameters in full expressions of the form of eqn [8] are still not commonly determined. These issues are discussed for olivine by Stocker (1978), Stocker and Smyth (1978), and Hirsch and Shankland (1993).

2.25.2.2 Effects of Temperature and Pressure

The Nernst–Einstein relation links the electrical conductivity to the diffusion coefficient of the charge-carrying species

$$\sigma = Dcq^2/(kT) \quad [9]$$

in which D is the self-diffusion coefficient, q is effective charge of the conducting species ($q=ze$, e is the charge of the electron and z is valence), c is the concentration of the conducting species, k is Boltzmann's constant, and T is temperature. The temperature dependence of electrical conductivity can arise from both the temperature dependence of concentration and thermally activated mobility. For thermally activated processes such as diffusion, $D=D_0 \exp(-E_a/kT)$. Thus, the temperature dependence of the conductivity will be of the form

$$\sigma = \frac{\sigma_o}{T} \exp(-E_a/kT) \quad [10]$$

in which σ_o is a preexponential constant and E_a is the activation energy. E_a is often expressed in electron volts eV; Boltzmann's constant k is equal to 8.617×10^{-5} eV (atom-deg)⁻¹. For many studies, the $1/T$ factor in the preexponential term on the right-hand side of eqn [9] is not used, especially if the studies are performed over a limited temperature range, so that expressions of the form

$$\sigma_i = \sigma_o \exp(-E_a/kT) \quad [11]$$

are employed. Plots of the logarithm of electrical conductivity versus $1/T$ that cover an extended range of temperature frequently show two (or more) linear regions or broadly curving regions. The variations in slope can be caused by transition from one dominant conducting species to another or by a transition from extrinsic (impurity dominated) to intrinsic conductivity. Each region is then described by an expression

of the form of eqn [11]. However, more precise and mechanistically more meaningful parameters are derived if the entire data set is simultaneously fit to a single expression of the form

$$\sigma = \sigma_{o1} \exp(-E_{a1}/kT) + \sigma_{o2} \exp(-E_{a2}/kT) \quad [12]$$

where subscripts 1 and 2 refer to the different mechanisms. Similarly, experiments covering a sufficiently wide range of f_{O_2} can express multiple mechanisms and be fit by expressions of the form

$$\sigma = \sigma_{o1} f_{\text{O}_2}^{n1} + \sigma_{o2} f_{\text{O}_2}^{n2} \quad [13]$$

The effect of pressure on conductivity can be characterized by the inclusion of an activation volume term ΔV_σ so that

$$\sigma = \sigma_o \exp(-[\Delta U_\sigma + P\Delta V_\sigma]/kT) \quad [14]$$

in which ΔU_σ is the activation internal energy and P is pressure. The term in the square brackets is the activation enthalpy H_σ . The activation volume is sometimes interpreted to indicate the volume of the mobile species, but such is not always the case. Commonly measurements at elevated pressures are parameterized isobarically as functions of temperature using eqn [10] or [11].

2.25.2.3 Electrical Conductivity of Olivine

2.25.2.3.1 Point defects in olivine

Olivine $(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$ is the dominant mineral between the bottom of the crust and the 410 km seismic discontinuity, comprising 40–60% by volume of the mantle in this depth range (Ringwood, 1975). Because of this abundance, it is one of the most frequently studied mantle minerals, but there are still nuances in its conductivity and point defect behavior that are not fully understood. We study olivine in detail because we need a complete understanding of the transport in order to extrapolate its behavior to conditions that have not been studied in the lab and because its behavior can inform us about other minerals.

The dominant charge-carrying defects in olivine are small polarons (Fe^{3+} on the Mg^{2+} lattice site $\text{Fe}_{\text{Mg}}^\bullet$), magnesium vacancies V_{Mg}'' , and electrons e' . There is general agreement that small polarons dominate at high f_{O_2} and lower temperatures, but there are disagreements at high temperature and lower f_{O_2} . The relationship describing the major defect populations and their f_{O_2} dependences in olivine (Schock et al., 1989; Stocker and Smyth, 1978) is



Studies on olivine have been performed on single crystals and polycrystalline aggregates and with self-buffering or pyroxene buffering of silica. If the cationic ratio Fe/Mg/Si is held fixed (i.e., for an experiment in which the olivine can exchange only oxygen with the environment and is not chemically in contact with other solid phases, termed the 'self-buffered' case) and at high f_{O_2} , the charge balance condition $4[V_{\text{Mg}}''] = [\text{Fe}_{\text{Mg}}^\bullet] = 8[V_{\text{Si}}''']$ pertains (Stocker, 1978) and evaluation of the equilibrium constant yields

$$[\text{Fe}_{\text{Mg}}^\bullet] = a_{\text{Fe}} f_{\text{O}_2}^{2/11} \quad \text{and} \quad [V_{\text{Mg}}''] = a_{\text{Mg}} f_{\text{O}_2}^{2/11} \quad [16]$$

where the 'a's' are constants. That is, the f_{O_2} dependences are identical. Potentially, one could distinguish the individual

contributions of Fe_{Mg} and V_{Mg}'' because they have individual concentration and mobility dependences on T and f_{O_2} , and this has been attempted in some instances.

For the pyroxene-buffered case, the f_{O_2} exponents are $n=1/6$ for both polarons and magnesium vacancies at high f_{O_2} (Stocker and Smyth, 1978). At low f_{O_2} , other defect interactions come into play that result in different f_{O_2} dependences for these and other defects (Hirsch and Shankland, 1993; Stocker and Smyth, 1978).

2.25.2.3.2 Electrical conductivity and anisotropy of olivine

Seminal studies by Duba et al. (1974) and Schock et al. (1989) paved the way for more recent studies of olivine electrical conductivity. Figure 1 shows log of conductivity versus f_{O_2} for single-crystal San Carlos olivine in the self-buffered case at 1200 °C. Three different sets of measurements are shown (Du Frane et al., 2005; Schock et al., 1989; Wanamaker and Duba, 1993). Agreement is good between these independent studies. The conductivity is greatest by up to a factor of 2 in the [00 1] orientation and approximately equal in the [10 0] and [01 0] directions. Conductivity increases with increasing oxygen fugacity, but the curves are not linear and the slope increases (i.e., f_{O_2} exponent n increases) with increasing f_{O_2} . At least two species or mechanisms are operative. Different researchers propose different models to explain these variations. Wanamaker and Duba (1993) concluded that Fe_{Mg} dominates at the highest f_{O_2} , with contributions from electrons e' (with an f_{O_2} exponent of $-1/6$) of greater importance at low f_{O_2} . Du Frane et al. fit their data using a non-differentiated model at high f_{O_2} (i.e., no distinction is made between Fe_{Mg} and V_{Mg}'' contributions because they have the same value of $n=+2/11$) with a contribution from a component with an f_{O_2} exponent of zero at low f_{O_2} , possibly from electrons or a background (extrinsic impurity) component. Each model fits the data over the f_{O_2} range it was collected, but each extrapolates to different values at the lowest f_{O_2} . Figure 2 shows the fits to these data sets with the two components for each fit.

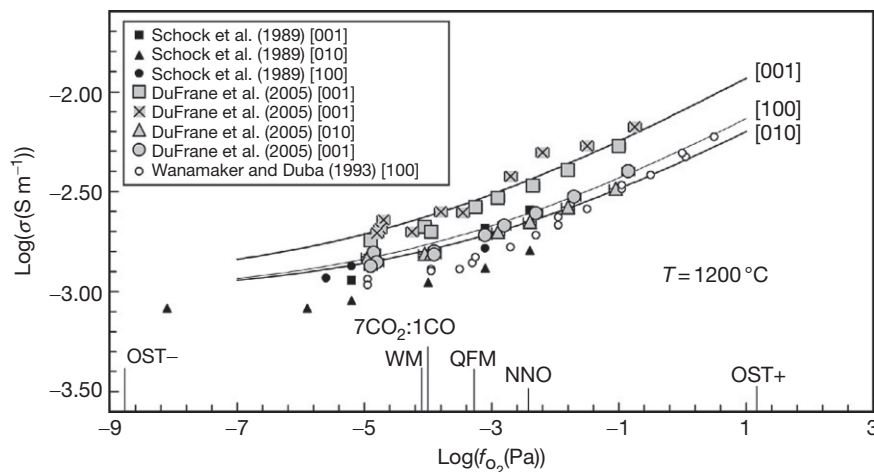


Figure 1 Olivine single-crystal conductivity in different orientations as a function of f_{O_2} for self-buffered experiments at 1200 °C. Large squares, triangles, circles, and solid lines, data and fits from Du Frane et al. (2005). Small filled squares, triangles, and circles; Schock et al., 1989. Open circles; Wanamaker and Duba, 1993. Schock and Wanamaker data are normalized to composition Fo89.1 using model of Hirsch et al. (1993). Adapted from Du Frane WL, Roberts JJ, Toffelmier DA, and Tyburczy JA (2005) Anisotropy of electrical conductivity in dry olivine. *Geophysical Research Letters* 32, L24315, <http://dx.doi.org/10.1029.2005GL023879>, with permission.

For the pyroxene-buffered case, point defect calculations indicate f_{O_2} exponents of $+1/6$ for both Fe_{Mg} and V_{Mg}'' at high f_{O_2} (Stocker and Smyth, 1978). At lower f_{O_2} , the situation is more complex and f_{O_2} exponents for $[V_{\text{Mg}}'']$ may be different. Figure 3 shows fits to electrical conductivity data for pyroxene-buffered olivine. The data and model of Wanamaker and Duba (1993) are for single-crystal olivine

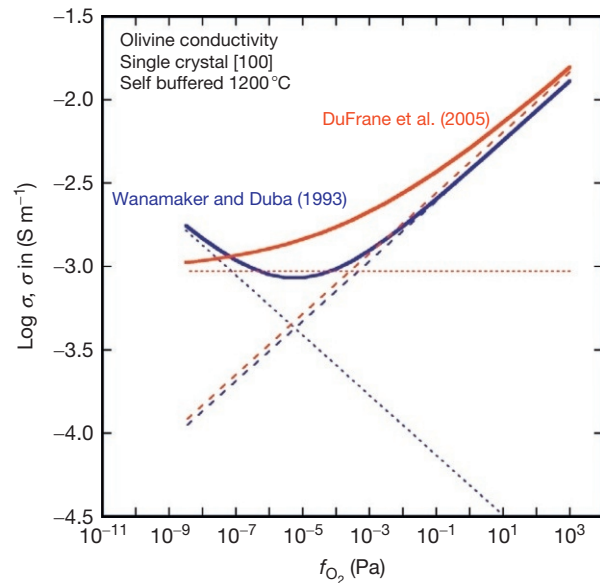


Figure 2 Models of olivine single-crystal self-buffered electrical conductivity at 1200 °C as a function of f_{O_2} in the [100] orientation. Blue lines: models of Wanamaker and Duba (1993). Red lines: Du Frane et al. (2005). Solid lines are the total conductivity. Long dashed lines represent the Fe_{Mg} polaron conductivity (Wanamaker and Duba, 1993) or the sum of polaron plus magnesium vacancy conductivity (Du Frane et al., 2005). Dotted lines represent electronic conduction (Wanamaker and Duba, 1993) or minimum (f_{O_2} independent) conductivity term (Du Frane et al., 2005).

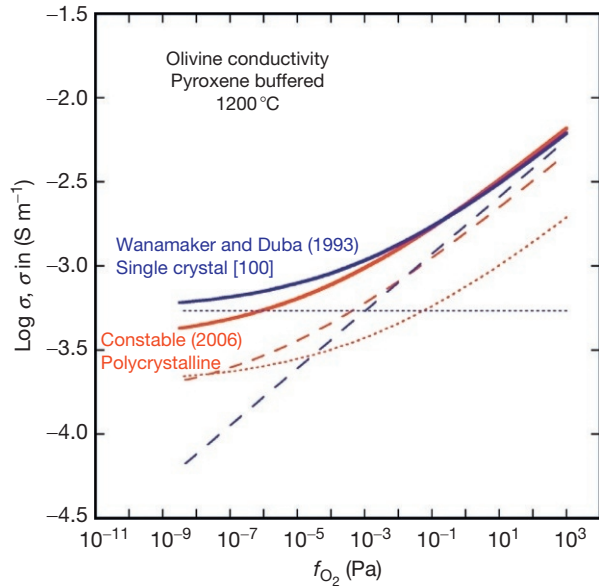
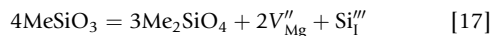


Figure 3 Models of pyroxene-buffered olivine electrical conductivity at 1200 °C as a function of f_{O_2} . Blue lines: model of Wanamaker and Duba (1993) for single-crystal olivine in [100] orientation. Red lines: model of Constable (2006), see also Constable and Roberts (1997), for polycrystalline olivine. Solid lines: total conductivity. Long dashed lines: Fe_{Mg} polaron conductivity. Short dashed lines: magnesium vacancy conductivity (Constable, 2006) or f_{O_2} independent term (Wanamaker and Duba, 1993).

in the [100] direction. The model of Constable (2006) (based on earlier results of Constable and Roberts (1997) is for polycrystalline olivine – this model is the successor to the SO_2 model of Constable et al. (1992)). Two different approaches are used in the fitting. Wanamaker and Duba fit the high f_{O_2} region with a Fe_{Mg} polaron with an exponent of 1/6, and the low f_{O_2} region with a model with an f_{O_2} exponent of zero that they ascribe to magnesium vacancies V''_{Mg} in a different charge neutrality regime. Constable and Roberts (1997) and Constable (2006) fit the data with a model in which the f_{O_2} exponents for both the Fe_{Mg} and V''_{Mg} concentrations are +1/6, but that includes a T-dependent empirical constant in the concentration term (of eqn [1]) that produces the flattening at low f_{O_2} . The Constable and Roberts (1997) and Constable (2006) model is derived from and fits both electrical conductivity and thermopower data. The thermopower data indicate a change in sign of the dominant species from positive to negative above about 1300 °C, consistent with V''_{Mg} dominated conduction. This change in the sign of the thermopower was first reported by Schock et al. (1989). Note that pyroxene-buffered olivine conductivity is lower by approximately 0.2–0.3 log units than the self-buffered case (Wanamaker and Duba, 1993). Concentrations of magnesium vacancies are higher in the pyroxene-buffered case because reactions, such as



where Me stands for Fe^{2+} or Mg^{2+} , cause increases in the number of magnesium vacancies, which causes lower concentrations of polarons and electrons through reaction [4].

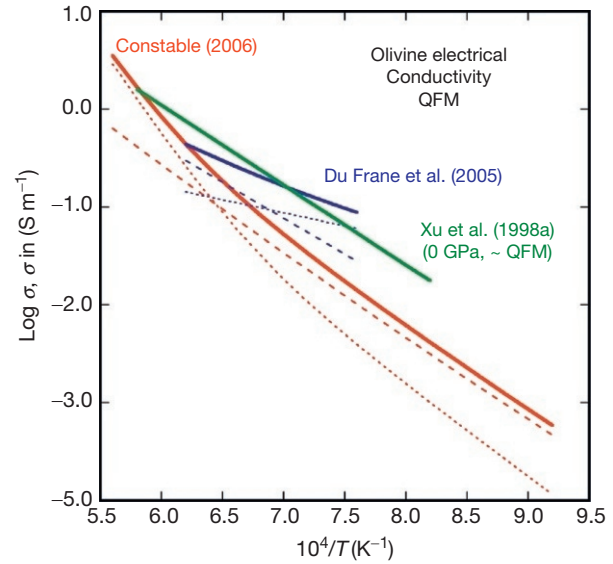


Figure 4 Electrical conductivity versus $1/T$ for several olivine models. Red lines: model of Constable (2006) along quartz–fayalite–magnetite (QFM) buffer – total conductivity (red solid line), polaron conductivity (red long dashed line), and magnesium vacancy conductivity (red dotted line). Blue lines: geometric mean model of Du Frane et al. (2005) along QFM buffer – total conductivity (blue solid line), polaron plus magnesium vacancy conductivity (blue long dashed line), f_{O_2} independent term (blue dotted line). Green line: high-pressure data of Xu et al. (1998a,b, 2000a,b) extrapolated to zero pressure and with factor of 0.25 log unit added to account for lower experimental f_{O_2} .

Figure 4 compares olivine $\log \sigma$ versus $1/T$ along the quartz–fayalite–magnetite (QFM) f_{O_2} buffer for the models discussed in the preceding text along with the zero-pressure conductivities of olivine of Xu et al. (1998a) (extrapolated from high-pressure measurements and adjusted for differences in experimental f_{O_2} ; see text later). The geometric mean of the Du Frane et al. model has a higher conductivity than the Constable and Roberts model, owing at least in part to the use of iron-doped platinum electrodes in these experiments. The high-pressure data of Xu et al. are collected along the Mo–MoO₂ buffer using molybdenum electrodes. Also shown are the conductivities corresponding to the individual mechanisms. At temperatures greater than about 1300 °C, the Constable (2006) model shows the increasing importance of magnesium vacancy conduction. The Du Frane et al. (2005) model indicates the dominance of the undifferentiated magnesium vacancy plus polaron term above about 1150 °C over the f_{O_2} independent term. Comparison of these studies indicates good experimental agreement and general agreement in the higher f_{O_2} ranges. Differences occur in the models developed to describe the low f_{O_2} behavior. Oxygen fugacity conditions in the Earth's mantle are generally thought to be in the range of the QFM buffer (see Figure 1). For these conditions, the models do not differ greatly.

The dependence of olivine electrical conductivity on total Fe content was examined by Hirsch et al. (1993). They found that conductivity varies as iron site fraction to the 1.81 power $[X_{Fe}]^{1.81}$, according to defect relations and eqn [7] or [8], indicating no effect on activation enthalpy. Karato and Wang

(2013) consolidated high-pressure results from a variety of experiments and minerals and concluded that in mantle minerals, conductivity σ is proportional to $\exp(\beta[X_{\text{Fe}}])$ where β is approximately 9, indicating either preexponential or activation enthalpy dependence on iron content. Yoshino et al. (2012) found that conductivity varies as iron site fraction to the first power $[X_{\text{Fe}}]$ and also that activation energy and activation volume decrease with increased iron content, which they attribute to small polaron hopping.

Grain boundary electrical conductivity has been considered by Roberts and Tyburczy (1991, 1993) and by ten Grotenhuis et al. (2004). Roberts and Tyburczy examined pressed sintered compacts of natural olivine with a $\sim 45 \mu\text{m}$ grain size and concluded that grain boundary and grain interior conductivities add in series, that is, that grain boundaries are not highly conducting paths. ten Grotenhuis et al. (2004) examined very fine-grained (1–5 μm) 95% forsterite–5% enstatite compacts and concluded that the bulk conductivity is controlled by grain boundary transport, that is, that the grain boundaries are highly conducting paths. The reasons for the differences between these results remain to be resolved.

2.25.3 High-Pressure Studies

2.25.3.1 Anhydrous Materials

Significant advances have been made in the determination of high-pressure electrical properties of mantle minerals. Xu et al. (1998a) determined the electrical conductivity of $\text{Mg}_0\text{Fe}_1\text{SiO}_4$ olivine, wadsleyite, and ringwoodite at pressures in their stability field under oxygen fugacity conditions similar to those of the mantle (Mo–MoO₂ buffer) using a multiple-anvil high-pressure device. Wadsleyite and ringwoodite exhibit conductivities 1–2 orders of magnitude greater than olivine. Pyroxene and higher-pressure polymorphs generally have conductivities lower than those of wadsleyite and ringwoodite and are comparable to olivine (Xu and Shankland, 1999). Perovskite, especially perovskite containing Al^{3+} , and magnesiowüstite (Mg,Fe)O have conductivities an order of magnitude or so higher than those of the transition zone phases (Xu et al., 1998b, 2000a,b; Xu and McCammon, 2002). Magnesiowüstite (with $\text{Fe}/(\text{Fe} + \text{Mg}) \sim 0.1$) conductivity is greater than perovskite conductivity with indications of a transition to a high-temperature mechanism at temperatures greater than about 1000 K at 10 GPa (Dobson and Brodholt, 2000; Dobson et al., 1997; Wood and Nell, 1991), although Xu et al. (2000a,b) did not observe such a variation. Activation volumes for conduction are relatively small for these materials. Olivine has the largest currently measured activation volume of $0.68 \text{ cm}^3 \text{ mol}^{-1}$ (Xu et al., 1998a, 2000a). Figure 5 shows a summary of the conductivities of these materials as a function of inverse temperature, all measured using the same techniques (Xu et al., 2000b). It is inferred that the dominant conduction mechanism in these phases is generally via $\text{Fe}_{\text{Mg}}^\bullet$ polarons, consistent with olivine conduction mechanisms. Mössbauer measurements of Fe^{3+} in these phases indicate much higher concentrations of Fe^{3+} than in olivine (O'Neill et al., 1993). In addition, the presence of Al^{3+} in silicate perovskite increases the amount of Fe^{3+} by a factor of 3.5 relative to Al^{3+} free perovskite (Xu et al., 1998b). In magnesiowüstite at high

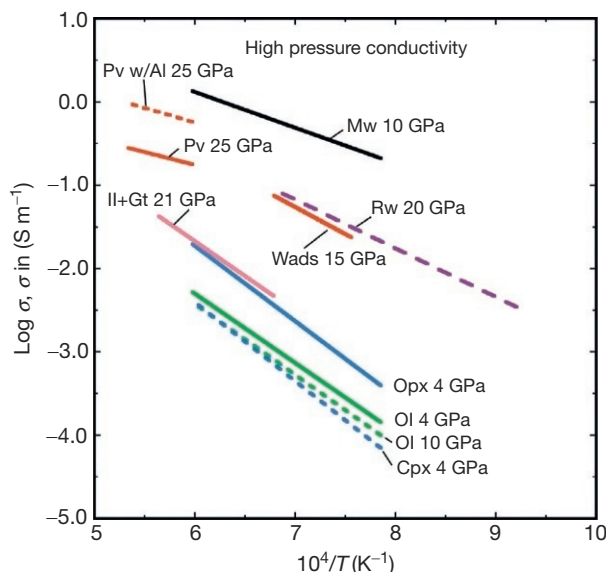


Figure 5 Electrical conductivity versus reciprocal temperature results for mantle minerals at high pressure and f_{O_2} representative of the mantle. Data are from multiple-anvil experiments of Xu and coworkers summarized by Xu et al. (2000a,b). Symbols: Pv, perovskite; Mw, magnesiowüstite; Rw, ringwoodite; Wads, wadsleyite; Il, ilmenite (akimotoite); Gt, garnet; Opx, orthopyroxene; Ol, olivine.

temperature, a large polaron mechanism in which holes in the valence band dominate conduction has been described (Dobson and Brodholt, 2000). Creation of a self-consistent data set permits calculation of mineral physics-based MT forward models that explicitly contain conductivity changes corresponding to the mineralogy changes at the major seismic discontinuities – see further discussion in the succeeding text.

2.25.3.2 Effects of Hydrogen

Karato (1990) calculated the electrical conductivity of hydrogen-bearing (also referred to as 'hydrous-') olivine using hydrogen chemical diffusion data (Kohlstedt and Mackwell, 1998) combined with the Nernst–Einstein equation (eqn [9]). Du Frane and Tyburczy (2012) expanded on these efforts by using more appropriate hydrogen self-diffusion data from deuterium–hydrogen exchange experiments with the resulting conductivity being slightly lower. This approach assumes that all the hydrogen present is free to contribute to the conductivity. Hydrogen diffusion in olivine is highly anisotropic so this approach predicts that the orientation dependence of hydrous olivine conductivity would be $\sigma_{[100]} \sim 20 \times \sigma_{[010]} \sim 40 \times \sigma_{[001]}$ (Constable, 1993; Karato, 1990), distinctly different than for dry olivine. Olivine sheared at low stress tends to line up with the $[100]$ orientation in the direction of shear. This explanation was used to infer that hydrogen-bearing oriented olivine was responsible for upper mantle electrical anisotropy near mid-ocean ridges (Evans et al., 2005), near the base of continental lithosphere (Bahr and Simpson, 2002), and electrical conductivity enhancement beneath the Pacific Ocean lithosphere (Lizzaralde et al., 1995).

High-pressure experimental techniques have been developed to measure conductivity of hydrogen-bearing mantle

minerals, but contrasting results have been obtained (Figure 6). Conductivity in a hydrous mineral can be expressed as

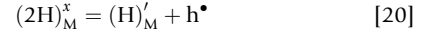
$$\sigma = \sigma_{\text{ion}} + \sigma_{\text{pol}} + \sigma_{\text{H}} \quad [18]$$

where σ_{ion} refers to (ionic) magnesium vacancy conductivity, σ_{pol} refers to conduction by $\text{Fe}_{\text{Mg}}^{\bullet}$ polarons, and σ_{H} refers to hydrogen-enhanced conductivity. Wang et al. (2006) examined conductivity of polycrystalline hydrous olivine at $P=4$ GPa and $T=873-1273$ K. Conductivity is strongly enhanced in the presence of hydrogen (water), and they used an expression of the form

$$\sigma_{\text{H}} = A_{\text{H}} C_{\text{W}}^r \exp(-H_{\text{H}}^*/RT) \quad [19]$$

where A_{H} and r are constants, C_{W} is water concentration and H_{H}^* is the activation enthalpy, to describe the results. For C_{W} expressed in weight percent water (H_2O), they determined that for olivine $A_{\text{H}} = 10^{3.0(0.4)} \text{ S m}^{-1}$, $r = 0.62 \pm 0.15$, and

$H^* = 87 \pm 5 \text{ kJ mol}^{-1}$ (Table 1). They concluded that although the most abundant site for hydrogen is as a neutral defect $(2\text{H})_{\text{M}}^{\times}$ corresponding to two protons trapped at a metal site (Kohlstedt and Mackwell, 1998; Kohlstedt et al., 1996), the electrical conductivity is governed by a concentration of free protons lower than the total concentration of hydrogen. The ionization reaction



predicts the exponent r will be between 0.5 and 0.75, depending on charge neutrality condition, which is close to their measured value. Thus, the Nernst–Einstein equation (eqn [9], for which $r=1$) may not apply directly if hydrogen speciation occurs (Karato, 2013). The activation enthalpy for conductivity in hydrogen-bearing samples is much lower than that of dry olivine. Activation energies for hydrogen diffusion are in the range 110–180 kJ mol^{-1} depending on orientation (Du Frane

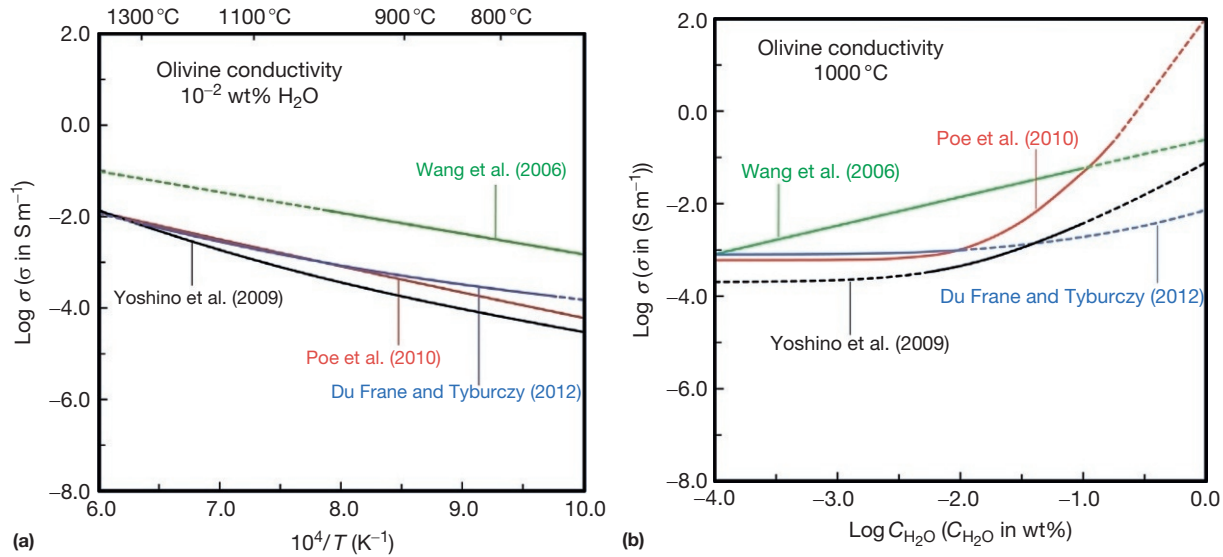


Figure 6 Electrical conductivity of hydrous olivine versus (a) reciprocal temperature for 10^{-2} wt% H_2O and (b) hydrogen content for 1000 °C. *In situ* measurements of σ from Wang et al. (2006) (solid green line), Yoshino et al. (2009) (solid black line), and Poe et al. (2010) (solid red line). Calculations of σ using hydrogen self-diffusion coefficient measurements from Du Frane and Tyburczy (2012) (solid blue line). Dashed lines indicate extrapolations from the range of conditions studied. Adapted from Du Frane WL and Tyburczy JA (2012) Deuterium-hydrogen interdiffusion in olivine: Implications for point defects and electrical conductivity. *Geochemistry, Geophysics, Geosystems* 13, 1–12.

Table 1 Conductivity models for hydrous olivine at elevated pressures of the general form $\sigma = \sigma_{\text{ion}} + \sigma_{\text{pol}} + \sigma_{\text{H}}$ (see text; error estimates listed if given)^a

Wang et al. 2006; $\sigma = A_{\text{pol}} \exp (-H_{\text{pol}}/kT) + A_{\text{H}} C_{\text{W}}^r \exp (-H_{\text{H}}/kT)$ C_{W} in wt% H_2O , $P = 4$ GPa						
A_{pol} (S/m)	H_{pol} (eV)	A_{H} (S/m)	r	H_{H} (eV)		
$10^{2.4}$	1.60	$10^{3.0(0.4)}$	0.62(0.15)	0.90(0.05)		
Yoshino et al. 2009; $\sigma = A_{\text{ion}} \exp (-H_{\text{ion}}/kT) + A_{\text{pol}} \exp (-H_{\text{pol}}/kT) + A_{\text{H}} C_{\text{W}} \exp (-H_{\text{H}} - \alpha C_{\text{W}}^{1/3})/kT)$ C_{W} in wt% H_2O , $P = 10$ GPa						
A_{ion} (S/m)	H_{ion} (eV)	A_{pol} (S/m)	H_{pol} (eV)	A_{H} (S/m)	H_{H} (eV)	α
$10^{4.73(53)}$	2.31(0.07)	$10^{2.98(0.85)}$	1.71(0.04)	$10^{1.90(0.44)}$	0.92(0.04)	0.16(0.02)
Poe et al. 2010 $\sigma = A_{\text{pol}} \exp (-H_{\text{pol}}/kT) + A_{\text{H}} C_{\text{W}} \exp (-H_{\text{H}} - \alpha C_{\text{W}}^{1/3})/kT)$ C_{W} in ppmw H_2O , $P = 8$ GPa						
Orientation	A_{pol} (S/m)	H_{pol} (eV)	A_{H} (S/m)	H_{H} (eV)	α	
[100]	334	1.46	$3.86(1.36) \times 10^{-2}$	1.26(0.04)	$5.49(0.20) \times 10^{-2}$	
[010]	13.8	1.12	0.290(0.061)	1.50(0.05)	$6.64(0.50) \times 10^{-2}$	
[001]	99.0	1.29	$1.04(0.22) \times 10^{-3}$	0.812(0.016)	$3.27(0.07) \times 10^{-2}$	

^aSubscripts: 'ion' indicates ionic, 'pol' is polaron, 'H' is hydrogen.

and Tyburczy, 2012; Kohlstedt and Mackwell, 1998). For bulk conductivity of olivine, Wang et al. (2006) developed a model incorporating polaron and hydrogen conductivity (Table 1).

Yoshino et al. (2006, 2009) examined conductivity of hydrous olivine and observed that the activation energy term for hydrogen conduction is concentration-dependent. They developed the following expression for hydrogen-enhanced conductivity:

$$\sigma_H = A_H C_W \exp \left(- \left(H_H - \alpha C_W^{1/3} \right) / RT \right) \quad [21]$$

where α is a constant. They ascribe the conduction to proton hopping, and this form of expression assumes that all the protons are equally mobile (the $C_W^{1/3}$ term suggests that hydrogen mobility depends on H–H distance, but does not indicate speciation). Conductivities are lower by 1–2 orders of magnitude than those of Wang et al. for the same water content. Yoshino et al. (2006, 2009) developed a conductivity model incorporating all three dominant defects; magnesium vacancies, polarons, and hydrogen-enhanced conductivity. Hydrogen conductivity dominates at the lowest temperatures, polaron conductivity dominates at intermediate temperatures, and magnesium vacancy conductivity dominates at the highest temperatures.

The two expressions used to fit conductivity measurements of hydrogen-bearing mantle minerals have different implications for conduction mechanism. Equations [19] and [20] suggest that only a subset of hydrogen atoms/ions exist as free protons that dominate conductivity. The concentration of free protons varies with water content, but not with temperature. Equation [21] suggests that all hydrogen contributes to conductivity, but activation enthalpy must be corrected for hydrogen concentration dependence. This reduction to activation enthalpy implies that even the highest water contents possible will not make large contributions to conductivity in the temperature range of the upper mantle. Poe et al. (2010) also examined conductivity of hydrous olivine at 8 GPa and obtained results more consistent with those of Yoshino et al. including preference for eqn [21] over eqn [19] to describe their data (Figure 6).

Results of Yoshino et al. (2006, 2009) and Poe et al. (2010) lead to the conclusion that hydrogen conduction is unable to account for high electrical conductivity anomalies observed in the mantle at asthenospheric depths, whereas Wang et al. (2006) values suggest that only 80 ppmw H₂O are needed to enhance olivine conductivity to asthenospheric values. This divergence in conclusion illustrates the importance of understanding the mechanisms of hydrogen-enhanced electrical conductivity. Jones et al. (2012) combined eqns [19] and [21] to yield

$$\sigma_H = A_H C_W^r \exp \left(- \left(H_H - \alpha C_W^{1/3} \right) / RT \right) \quad [22]$$

and used observed conductivities from MT studies and mantle water content estimates (from xenoliths) beneath the mantle water content estimates to fit eqn [22]. However, fits yielded a broad range of solutions for parameters r and α . Khan and Shankland (2012) used the various laboratory data available to constrain fits of geophysical data to estimate major element chemistry and water content beneath continents.

The electrical conductivity of hydrogen-bearing single-crystal olivine in different orientations was examined at 3 GPa and T between 500 and 1000 K (Yoshino et al., 2006) and at 8 GPa and T between 773 and 973 K (Poe et al., 2010). Conductivity is enhanced by about 1–2 orders of magnitude over that of anhydrous olivine and anisotropy is consistent with diffusion directions with $\sigma_{[100]} > \sigma_{[010]} > \sigma_{[001]}$ at constant hydrogen content. Yoshino et al. fitted activation enthalpies of $H_{[100]} = 70 \text{ kJ mol}^{-1}$, $H_{[010]} = 90 \text{ kJ mol}^{-1}$, and $H_{[001]} = 84 \text{ kJ mol}^{-1}$. However, extrapolated to slightly higher temperatures of 1273 K, the conductivity of hydrogen-bearing olivine becomes nearly isotropic, whereas at the same temperature, hydrogen diffusivity is strongly anisotropic. Yoshino et al. interpreted this difference to indicate different mechanisms for hydrogen mobility in diffusion and conductivity. Poe et al. fitted activation enthalpies of $H_{[100]} = 122 \text{ kJ mol}^{-1}$, $H_{[010]} = 145 \text{ kJ mol}^{-1}$, and $H_{[001]} = 78 \text{ kJ mol}^{-1}$, which are only slightly lower ($\sim 30 \text{ kJ mol}^{-1}$) than those measured for hydrogen diffusion (Du Frane and Tyburczy, 2012; Kohlstedt and Mackwell, 1998).

Hydrogen may affect other charge-carrying defects in olivine. Calculations based on density functional theory indicate that hydrogen creates an impurity level in the electronic band-gap of olivine (Wang et al., 2011, 2012). It is unknown whether this causes an electronic conductivity sufficiently large to affect the overall electrical properties of olivine. Hier-Majumder et al. (2005) measured Mg–Fe interdiffusion in hydrous olivine and found a small enhancement in the presence of water, but not sufficient to yield a conductivity increase of the magnitude measured for hydrous olivine.

These topics have been discussed by Yoshino (2010), Karato and Wang (2013), Pommier (2013), and Yoshino and Katsura (2013).

2.25.4 Electrical Conductivity of Melts and Partial Melts

Naturally occurring silicate melt conductivity has been examined at elevated pressure in dry systems to 2.5 GPa (Tyburczy and Waff, 1983, 1985) and in a hydrous silicic melt to 0.4 GPa (Gaillard, 2004). Conductivity of a basaltic melt decreases with increasing pressure up to about 0.8 GPa and then is independent of pressure to 2.5 GPa (Tyburczy and Waff, 1983). Dry silicic melts have greater pressure dependence, with activation volumes on the order of a few $\text{cm}^3 \text{mol}^{-1}$ at 2.5 GPa (Tyburczy and Waff, 1985). Gaillard (2004) examined conductivity of an obsidian melt with up to 3 wt.% water and found an increase of about $\frac{1}{2}$ order of magnitude or less over the dry obsidian at 0.2 GPa corresponding to an activation volume of about $20 \text{ cm}^3 \text{mol}^{-1}$. Pommier et al. (2008) studied dry and hydrous melts from Mt. Vesuvius with similar results. Pommier and Le-Trong (2011) developed a method for calculation of natural silicate melt conductivity as a function of SiO₂, Na₂O, H₂O, T , and P . Conductivities of molten carbonates are 100–1000 times greater than those of molten silicates with much lower activation energies (Gaillard et al., 2008).

Waff (1974) discussed the importance of the textural distribution of melt on the bulk electrical properties of a partially molten rock and the importance of textural equilibration

(Bulau et al., 1979). Studies of texturally equilibrated partially molten systems include those of Roberts and Tyburczy (1999) and ten Grotenhuis et al. (2005). Roberts and Tyburczy (1999) showed that for an Fo₈₀-melt system, the melt was highly interconnected at low melt fractions (0–5 vol.%) and that parallel-type bulk conduction models (Hashin–Shtrikman upper bound, simple parallel conductors, or Archie’s law) describe the data (see text later). Archie’s law ($\sigma_{\text{bulk}}/\sigma_{\text{melt}} = CX^m$, where C and m are constants and X is volume fraction melt) constants $C=0.73$ and $m=0.98$ were determined. They pointed out that melt composition changes significantly with changes in melt fraction at very low melt fractions and that these changes may need to be considered when modeling low melt fraction systems. ten Grotenhuis et al. (2005) examined an iron-free olivine–enstatite–melt system and observed a change from nearly dry grain faces (with melt mostly in tubules or triple junctions) at 1 vol.% melt to mostly wetted grain faces at a melt fraction of 10 vol.%. The change was discontinuous, with the most abrupt change occurring at around 2 vol.% melt. They determined Archie’s law constants of $C=1.47$ and $m=1.30$. Caricchi et al. (2011) examined the effect of torsional deformation on electrical conductivity of a partially molten olivine–melt system. Conductivity is enhanced (melt is interconnected) in the direction of maximum shear and is lower (melt is not interconnected) perpendicular to maximum shear (i.e., radially in the torsion experiment) consistent with melt segregation studies (King et al., 2010). Such anisotropy of melt distribution and bulk conductivity could explain anisotropy of conductivity parallel and perpendicular to mid-ocean ridges (Baba et al., 2006; Caricchi et al., 2011).

2.25.5 Mixing Relationships

The bulk conductivity of a rock consisting of several minerals depends on the textural distribution of the minerals, which is generally not well known. A variety of relations have been employed to do so. Series and parallel solutions yield the maximum and minimum values, respectively, of a mixture of materials

$$\sigma_s^{-1} = x_1/\sigma_1 + x_2/\sigma_2 \quad [23]$$

$$\sigma_p = x_1\sigma_1 + x_2\sigma_2 \quad [24]$$

where σ_s is the series conductivity, σ_p is the parallel conductivity, σ_1 and σ_2 are the conductivities of the constituent phases, and x_1 and x_2 are the volume fractions. The geometric mean conductivity σ_{GM} is given by

$$\sigma_{\text{GM}} = \sigma_1^{x_1} \sigma_2^{x_2} \quad [25]$$

Archie’s law (Archie, 1942) is often used for fluid- or melt-rock mixtures

$$\sigma_{\text{bulk}}/\sigma_{\text{melt}} = CX^m \quad [26]$$

where σ_{bulk} is the conductivity of the mixture, C and m are constants, and x is volume fraction melt or fluid. For very low porosities, a modified expression is used (Hermance, 1979)

$$\sigma_{\text{bulk}} = \sigma_{\text{rock}} + (\sigma_{\text{fluid}} - \sigma_{\text{rock}})x^m \quad [27]$$

The Hashin–Shtrikman bounds describe the narrowest upper and lower bounds in the absence of geometric information (Hashin and Shtrikman, 1962)

$$\sigma_{\text{HS}+} = \sigma_1 + x_2[(\sigma_2 - \sigma_1)^{-1} + x_1/(3\sigma_1)]^{-1} \quad [28]$$

$$\sigma_{\text{HS}-} = \sigma_2 + x_1[(\sigma_1 - \sigma_2)^{-1} + x_2/(3\sigma_2)]^{-1} \quad [29]$$

where $\sigma_1 > \sigma_2$, and $\sigma_{\text{HS}+}$ and $\sigma_{\text{HS}-}$ correspond to the upper and lower bounds, respectively. The effective medium bounds (Landauer, 1952) lie between the HS upper and lower bounds

$$\sigma_{\text{EM}} = \frac{1}{4}\{(3x_1 - 1)\sigma_1 + (3x_2 - 1)\sigma_2 + [(3x_1 - 1)\sigma_1 + (3x_2 - 1)\sigma_2]^2 + 8\sigma_1\sigma_2\}^{1/2} \quad [30]$$

These and other relationships have been applied to the conductivities of multiphase materials in the mantle (e.g., Xu et al., 2000a,b) including partial melts. They yield the widest ranges when the conductivities of the two phases in question are greatly different, for example, in the transition zone (Xu et al., 2000a,b) or for partial melts.

2.25.6 Application to MT Studies

We discuss here a small number of MT field studies as representative of those for which these laboratory results have been influential in modeling or interpreting mantle conditions. In MT studies, orthogonal components of electrical E_x and magnetic H_y fields as a function of period τ are measured at the Earth’s surface. From these, the apparent resistivity $\rho(\tau)$ and phase $\varphi(\tau)$ are determined according to

$$\begin{aligned} \rho(\tau) &= (\tau/2\pi\mu) (E_x/H_y)^2 \quad \text{and} \quad \varphi(\tau) \\ &= \tan^{-1}(E_x/H_y) \end{aligned} \quad [31]$$

where μ is the magnetic permeability (Cagniard, 1953; see Simpson and Bahr, 2005 for a recent discussion of MT methods). Conductivity–depth models are fit to or derived from such field results using smooth or discontinuous models. The D+ inversions provide the best fitting model to the data $\rho(\tau)$ and $\varphi(\tau)$ that can be achieved; they consist of a series of delta functions in conductivity as a function of depth (Parker, 1980). Occam’s razor inversions yield the smoothest possible conductivity–depth models to the data (Constable et al., 1987). Neither of these approaches corresponds to a real physical Earth. The existing framework of experimental results on electrical conductivity of Earth materials under mantle conditions allows for modeling and interpretation of electromagnetic field results in terms of realistic mineralogies reflecting known seismic discontinuities and mantle conditions.

Xu et al. (2000b) showed that using their nominally anhydrous laboratory data, a mineral physics-based conductivity–depth model for the upper mantle and transition zone provides a very good fit (via forward modeling) to resistivity $\rho(\tau)$ and phase $\varphi(\tau)$ for a European MT data set (Olsen, 1999) (Figure 7). This agreement indicates that the laboratory data provide a robust framework for interpreting MT results. Note, however, that recent experimental results on water-containing minerals indicate that some of the earlier nominally anhydrous experiments contained significant amounts of hydrogen (Huang et al., 2005). Other models based on MT studies include effects of water in mantle and transition zone minerals (Karato, 2006; Lizzaralde et al., 1995; Simpson and Tommasi,

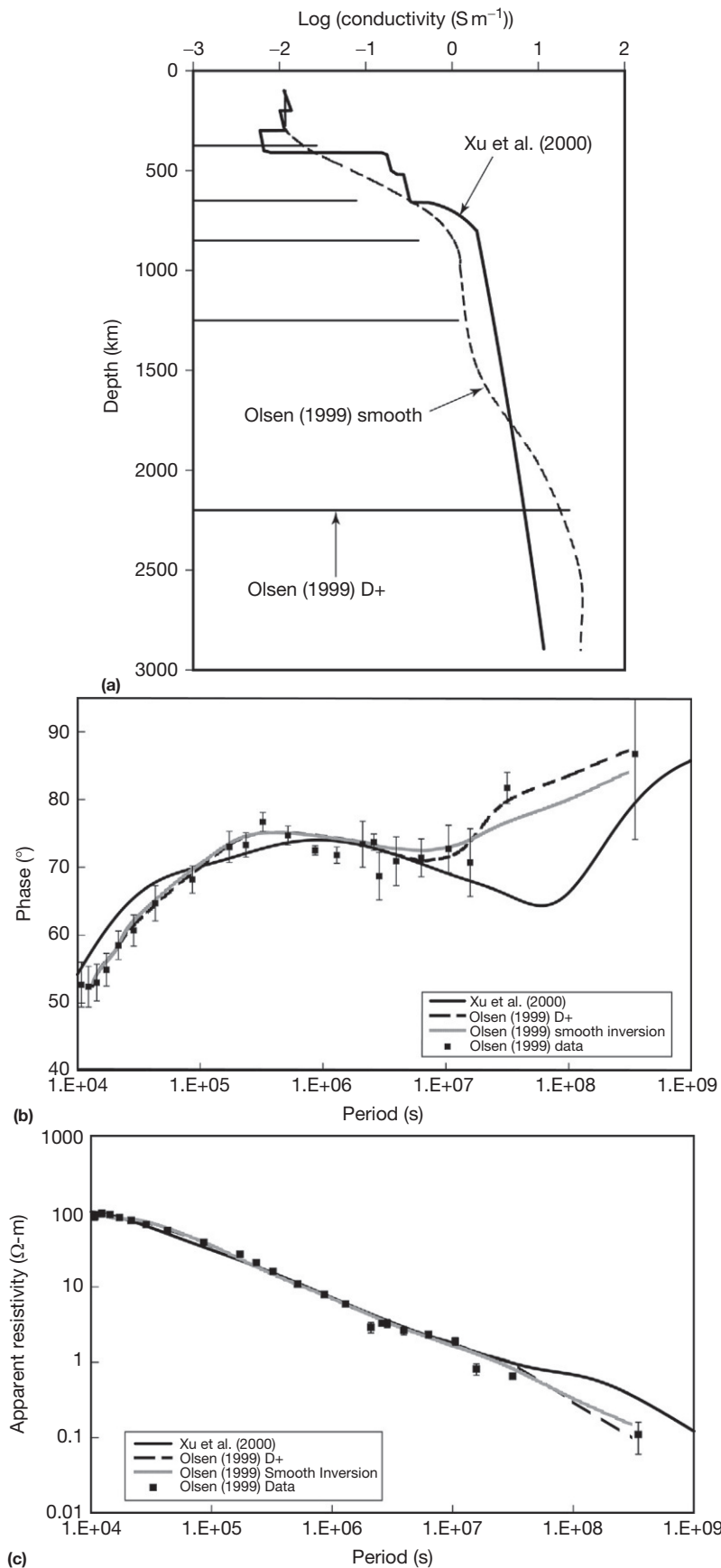


Figure 7 (a) Electrical conductivity versus depth profile for Europe from Olsen (1999) with D+ and smooth inversions and mineral physics-based model of Xu et al. (2000a,b). Smooth inversion is from Tarits et al. (2004). (b) Phase and (c) apparent resistivity as a function of frequency data and the models. Adapted from Xu YS, Shankland TJ, and Poe BT (2000b) Laboratory-based electrical conductivity in the earth's mantle. *Journal Geophysical Research* 105, 27865–27875; Tarits P, Hautot S, and Perrier F (2004) Water in the mantle: Results from electrical conductivity beneath the French Alps. *Geophysical Research Letters* 31, L06612, <http://dx.doi.org/10.1029/2003GL019277>, with permission.

2005; Tarits et al., 2004). There are significant regional differences in transition zone conductivity that may be attributable to variations in water content (Karato, 2006; Tarits et al., 2004). Conductivity–depth profiles as a function of water content down to the mantle transition zone have been published based on widely varying laboratory measurements on hydrous minerals (Jones et al., 2012; Karato, 2011; Khan and Shankland, 2012).

Just off of the southern East Pacific rise, Evans et al. (2005) observed strong electrical conductivity anisotropy at a depth of 100 km, with the ridge perpendicular (plate motion parallel) value approximately a factor of 10 greater than the ridge parallel value. They interpreted this result using the earlier diffusion-based model of hydrogen-enhanced olivine conductivity to indicate hydrous (10^3 H/ 10^6 Si) shear-oriented olivine ([100] parallel to flow direction, perpendicular to the ridge). However, Yoshino et al. (2006) pointed out that their the high-pressure conductivity measurements indicate a much smaller amount of electrical conductivity anisotropy in hydrous olivine, suggesting that partial melt may be the cause of the conductivity anisotropy near the ridge.

2.25.7 Summary

Many aspects of the electrical conductivity of mantle minerals and its dependence on environmental factors are well measured and understood. Laboratory measurement of electrical conductivity of mantle and transition zone minerals has advanced to the point where interesting and provocative interpretations of mantle MT profiles in terms of mineralogy, temperature, composition, and water content are possible. The coming years promise significant new revelations from the study of electrical properties of Earth materials and the application to Earth interior issues.

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